Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC020101

FWP and possible subtask under FWP: FWP Microscopy and Microanalysis

FWP Number: ERKCM03

Program Scope: The Microscopy and Microanalysis task involves operation and development of the SHaRE Collaborative Research Center and User Program (www.ornl.gov/share), applications to materials science, and research collaborations in the areas of analytical transmission electron microscopy (TEM) and scanning electron microscopy (SEM), atom-probe field-ion microscopy (APFIM), and mechanical properties microprobes (MPM).

Major Program Achievements (FY2000 – FY2002): Co-hosted two workshops to develop vision and community support for the transmission electron aberration-corrected microscope (TEAM) development project, a major new initiative in electron microscopy; specified and ordered unique new facility instrumentation: local electrode atom probe (LEAP) and low voltage microprobe (LVM) with bolometer energy-dispersive X-ray (EDX) spectrometer; published book on atom probe tomography (APT); developed methods to quantify size, shape, and composition of nanometer-scale microstructural features characterized by small clusters of atoms, as determined by APT, and for quantitative comparison of APT and small-angle neutron scattering (SANS) measurements; developed new analytical methods for measuring residual stress by nanoindentation with spherical indenter, correlating indentation size effects for spherical and sharp indenters, and elastic displacement of thin-film-on-substrate systems during nanoindentation; development and refinement of variety of analytical electron microscopy (AEM) techniques, including energy-filtered TEM, ALCHEMI, low-voltage EDX, spectrum imaging, and orientation imaging microscopy (OIM); numerous applications.

Program Impact (FY2000 – FY2002): Microscopy community endorsement and sponsor support of TEAM development project; new microcharacterization methods and instrumentation developed in analytical electron microscopy, atom probe tomography, and mechanical properties microprobes; widespread and broad-based impact of SHaRE Facility and User Program; 16 PhD and two MSc theses completed by SHaRE Program participants.

Interactions (FY2000 – FY2002): SHaRE Facility usage includes:
Institutions: 37 US universities; 13 companies; 6 DOE national laboratories; 4 non-DOE national laboratories.
Funding agencies: DOE-Fusion Energy Sciences, DOE-Advanced Scientific Computing, DOE-SC LTR CRADA; DOE-Fossil Energy, DOE-Energy Efficiency and Renewable Energy; NASA, DARPA; ORNL-LDRD.

Recognitions, Honors and Awards (FY2000 – FY2002):
Anderson: Presidential Early Career Award for Scientists and Engineers (PECASE), 2001; Director of Microbeam Analysis Society (MAS), 1999-2001; MAS Liaison to Microscopy and Microanalysis meetings, 2001-present; MAS Co-Chair, Microscopy and Microanalysis 2004; Chair, ASM Action-in-Education Team, 2000-2002; Oak Ridge Chapter of ASM, 2002-2003; Education and Program Committees of the Microscopy Society of America (MSA)

Bentley: Scientific Editor, J. Microscopy, 1999-2000; Editorial Boards of Microscopy and Microanalysis, Microscopy and Analysis, ongoing; Chair, Awards Committee of MSA, 2001-present; Symposium Organizer, Fall 1999 MRS Meeting, Spring 2001 MRS Meeting, and 15th International Congress on Electron Microscopy, 2002
Kenik: 2002 Warren F. Savage Memorial Award, American Welding Society
Miller: Editorial board, J. Microscopy, ongoing; Editor, special issue of Materials Characterization, 2000
Pharr: ISI Citation Classic (1000+), 2002; University of Tennessee Science Alliance Award for Research Achievement, 2001; Associate Editor, J. Am. Ceram. Soc., ongoing; Volume Organizer, MRS Bulletin, 2000; Chair, 2000 Gordon Conference on "Thin Film Mechanical Behavior"

Personnel Commitments for FY2002 to nearest +/- 10%:
I.M. Anderson (80%), J. Bentley (90%), E.A. Kenik (70%), M.K. Miller (70%), K.F. Russell (70%), K.A. Thomas (20%); N.D. Evans (ORISE, 100%), G.M. Pharr (U Tennessee, 40%), A. Rar (Postdoctoral Fellow, 100%)

Authorized Budget (BA) for FY00, FY01, FY2002 (*includes ORISE SHaRE Program FWP):
FY00 BA $2013k* **FY01 BA $**2000k* **FY02 BA $**2010k

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0201010

FWP and possible subtask under FWP:
Atomistic Mechanisms in Interface Science—Direct Imaging and Theoretical Modeling

FWP Number: ERKCS30

Program Scope: Atomic resolution Z-contrast scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) are combined with first-principles theoretical calculations to determine atomic configurations, impurity segregation energies and sites and diffusion pathways at critical sites in materials and nanostructures.. Problems are tackled that cannot be treated by either technique alone, for example, unexpected atomic configurations are seen by experiment, which theory then uses to explain properties. This approach is applied to ceramics, high Tc superconductors, complex oxides, metals and alloys, and a large variety of grain boundaries, interfaces and superlattices.
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Major Program Achievements (over duration of support): The origin of electrical activity was identified in $SrTiO_3$ grain boundaries as non-stoichiometry. Grain boundaries had traditionally been thought to maintain stoichiometry and structural models had always assumed stoichiometry. These results showed the reverse to be the case. Grain boundaries in oxides are generally non-stoichiometric and have associated electrical activity and special sites. This can be the source of useful effects (varistor action, electrical capacitance, thermistor behavior, low field colossal magnetoresistance) but also may be bad (low critical currents in high Tc oxides). Results appeared in Science and Physical Review Letters. The reason for the embrittlement of grain boundaries in copper by impurities such as bismuth was determined. Electrons from the bismuth spread into the copper giving it the mechanical properties of zinc, the classic ductile solid. Results are submitted to Nature. Studies of decagonal quasicrystals revealed for the first time that the origin of their quasi-periodic arrangement lay in a broken symmetry at a specific point in their structure. A huge driving force existed for chemical ordering that drives the whole structure into this unusual arrangement. Results appeared in Nature and Physical Review Letters. First observation of a grain boundary structural transformation driven by impurity segregation, appeared in Physical Review Letters. The structure of gamma alumina was shown to be a sequence of hydrogen containing compounds, in which the hydrogen is mobile and can exchange with surface aluminum. This resolved 50 years of controversy over the structure, explained the distinct surface chemistry of the gamma phase, the very different catalytic activity of the eta phase, and showed that platinum clusters actually nucleate in surface vacancies where they have unusual catalytic activity. Results published in Journal of the American Chemical Society and Surface Science Letters.

Program Impact: Program has contributed to the commercial development of atomic resolution STEM and the explosion in purchases by materials science departments in the US and worldwide. Instruments are now available from two major overseas companies and a US startup company. Program generated 6 articles in Nature or Science and 23 Physical Review Letters.

Interactions: Vanderbilt University, North Carolina State University, University of Illinois at Chicago, University of Cambridge, Northwestern University, University of Florida, University of

Pennsylvania, National Institute for Materials Research, Japan, Dartmouth College, Massachusetts Institute of Technology.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Institute of Physics Thomas Young Medal awarded to S. J. Pennycook and Fellowship of The Institute of Physics. Results are featured in an average of 25 invited talks per year and numerous book chapters

Personnel Commitments for FY2002 to Nearest +/-10%:
S. J. Pennycook (group leader) 20%
S. T. Pantelides (Distinguished guest scientist at ORNL) 5%
M. F. Chisholm 50%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $ 675k **FY01 BA $** 628k **FY02 BA $** 615k

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0201010

FWP and possible subtask under FWP:
Theoretical Studies of Metals, Alloys, and Ceramics

FWP Number: ERKCM01

Program Scope: The development and use of first principles quantum mechanical calculations to predict materials properties, to relate them to the electronic structure, and to guide materials design.

Major Program Achievements (over duration of support): Pioneered the development of the first principles KKR-CPA theory of the electronic structure and properties of substitutionally disordered alloys as well as electronic structure based theories of clustering, ordering, and alloy phase stability.

Pioneered the use of the highly accurate FLAPW calculations of the properties of intermetallic compounds including, structure, elastic properties, energies of defects, planar faults, and interfaces, and thermal expansion to predict mechanical behavior and to guide experimental alloy development.

Developed the precise PWSCF cluster technique for studying microchemical effects in intermetallic alloys and ceramics. Pioneered the use of these first principles techniques in the study of intergranular phases and dopant effects and to guide the development new structural ceramics.

Pioneered the application of first principles electronic structure methods to the understanding of spin transport and spin tunneling in GMR multilayers and related systems.

Developed a linear scaling first principles electronic structure method for application on massively parallel supercomputers that now allows first principles spin dynamics calculations of complex non-collinear magnetic structure in alloys, inhomogeneous systems and nano-structures.

Program impact: FLAPW calculations have supported alloy design of Ni-, Fe-, and Ti-based aluminides, and Mo-, Ti-based silicides, have provided basic understanding of defect-formation mechanisms and thermal elastic properties of these alloys and have set the standard for first-principles calculations of ordered intermetallics.

Our first-principles PWSCF studies support the structural ceramics task and have provided a basic understanding of mechanical properties of silicon nitride ceramics.

The KKR-CPA is used throughout the world for calculating the electronic structure of substitutionally disordered systems and many of these codes had their genesis in the ORNL codes.

Interactions: ORNL: CCS-CMR, SNS; CSM- and SS- Divisions; ABAD-, NDE-, X-ray Res. and Appl., and Structural Ceramics Groups. External: Ames Lab., LANL, LBNL, Florida Atlantic Univ., Col. School of Mines, Tulane Univ., MINT-Center Univ. Alabama; DRAL – Daresbury, UK; Univ. Bristol, UK; Univ. Messina, Italy; Kyoto, Japan; Res. Inst. for SS Phys, Budapest; CCMS Tech. Univ.Vienna; Computational Materials Sciences Network (CMSN). Industry: Honeywell SS Electronics Center, Motorola Corp. Res. Lab., and IBM Almaden Res. Center. CRADAs: IBM, Honeywell, Motorola, and Nonvolatile Electronics, Inc.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): C. L. Fu: 1991 US-DOE DMS Outstanding Scientific Accomplishment (1991); Listed on ISI 1000 Most Cited Physicists; 2002 TMS Champion H. Mathewson Medal. G. S. Painter: APS Fellow, Martin Marietta Energy Systems Awards (1987; 1988, 1989, 1994). G. M. Stocks: APS Fellow, Gordon Bell Prize {1998, 1990, 2001 – Hon. Men.)}, Computerworld Smithsonian Laureate (2000), Martin Marietta Energy Systems Awards (1992, 1986)}, Cray Research Giga-flop Award (1990); US-DOE DMS Award for Outstanding Sustained Research in Metallurgy and Ceramics (1989; 1983 – with W. H. Butler and J.S. Faulkner)

Personnel Commitments for FY2002 to Nearest +/- 10%:
G. M. Stocks (70%), C.-L. Fu (90%), G. S. Painter (80%), Postdoctoral Staff (50%), Support Staff (60%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $ 797k **FY01 BA** $ 790k **FY02 BA** $875k

Oak Ridge National Laboratory
B&R Code: KC0201020

FWP: Microstructural Design of Advanced Ceramics

FWP Number: ERKCM07

Program Scope: Theory and experiment combine to define (1) the relationships between the properties of ceramics and the critical length-scale structural characteristics and (2) how these can be tailored during processing. This approach then incorporates different length-scale characteristics into analytical models that are used to tailor the mechanical behavior (e.g., toughness, mechanical reliability, creep resistance) and electrical conductivity of ceramics. The results provide a quantitative picture of the mechanisms that toughen ceramics and enhance the mechanical reliability of multilayer systems and coatings so as to overcome the brittleness of these systems.

Major Program Achievements: Leaders in the development of microstructural design concepts for ceramic systems that provides a sound fundamental basis for tailoring their properties. Revealed importance of internal stresses derived from mismatch in properties in (1) the processing and properties of multiplayer systems and (2) fracture toughening processes in ceramics. Lead the development and fundamental understanding of ceramics reinforced with microscopic whiskers for substantially improved mechanical performance. Uncovered the importance of the composition of grain boundary films in dictating the toughness and mechanical performance of advanced ceramics and collaborated on establishing first principals theoretical studies that reveal the relationship to the nature of the chemical bonds.

Program impact: Provided insights into the microscopic origins of the mechanical behavior of ceramics that have lead to toughened ceramics and novel design concepts for tailoring ceramic properties that are now being extended to include the role of atomic-level, as well as microscopic, characteristics. The whisker-reinforced ceramics developed also have had a significant economic impact with the establishment of an annual market of >$30M in cutting tools and metal forming tooling.

Interactions:
Internal–Metals and Ceramics Division: Theory Group, Microscopy Microanalytical and Microstructure Group, Solid State Division: Thin Film and Nanostructured Materials Physics Group.
External–University of Karlsrühe, AIST Synergy Ceramics Center; University of Tokyo, Max Planck Institute for Materials Research, Korea Institute of Machinery and Materials, National Tsing Hua University, Kyoto Institute of Technology, United Technologies Research Center, Dupont Central Research Laboratory.

Recognitions, Honors and Awards:
Alexander Von Humboldt Foundation Research Award for Senior Scientists
American Ceramic Society: Purdy Publication Award, Sosman Memorial Lecturer, Society President.
International Inventors Hall of Fame Advanced Technology Award
Federal Laboratories Consortium Special Award of Excellence
DOE Office of Basic Energy Sciences, Materials Sciences Division Research Award
Composite Engineering Editorial Board & Associate Editor Journal of the American Ceramic Society
Japan Science and Technology Cooperation Science and Technology Agency Fellowship Award
Wigner Fellow
Advisory Board of the Europhysics Conference on Defects in Insulating Materials
Organizing committee of five international conferences since 2000
Ten invited lectures at international technical conferences since 2000

Personnel Commitments for FY2002:
P. F. Becher (group leader) 70%; Chun-Hway Hsueh 90%; Igor Kosacki 90%; Michael J. Lance 30%

Authorized Budget (BA):
FY00 BA $1037k **FY01 BA $1092k** **FY02 BA $948k**

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0201020

FWP and possible subtask under FWP: FWP Acoustic Harmonic Generation by Microstructures

FWP Number: ERKCM21

Program Scope: First-principles calculations are being used to characterize the interaction of elastic waves with microstructure and to provide the necessary background for interpreting the experimental work. Concomitantly, target alloy specimens are being fabricated with the very high purity and density necessary to isolate the microstructural feature of interest for analysis. Both the linear and nonlinear responses of the microstructure are then examined experimentally in order to compare with the calculations and to assess the ability of these measurement techniques to detect and quantify early-stage microstructural degradation.

Major Program Achievements (over duration of support): This research has uncovered an inaccuracy in the long-accepted theory describing elastic wave scattering from microstructures and has developed a new theory that challenges the nature of this scattering in the long-wavelength regime. Experimental confirmation obtained on this program has shown that the scattering scales quadratically with frequency and linearly with grain size in the Rayleigh regime, in contrast to the accepted formulation, which predicts fourth-power dependence on frequency and third-power dependence on grain size. In addition, first-principles calculations predict, and measurements of elastic nonlinearity confirm, that solid solution has only a small effect on elastic nonlinearity. The effects of additional microstructural features are now being assessed

Program Impact: The results on elastic scattering will have major impact both on our understanding of this phenomenon and on the practical applications of elastic scattering to material characterization. For example, scattering losses in the high-frequency regime have been related to microstructural degradation for some materials, and this work extends the applicability of this approach to the long-wavelength regime as well. In addition, the work in elastic nonlinearity will have a major impact on our ability to assess early-stage microstructural degradation in materials nondestructively, when the features that may dominate failure, e.g., the formation of precipitates, creep voids, dislocation networks, etc., are still very small with respect to the dominant scatters, viz., grains, in the material and thus are undetectable by present nondestructive approaches.

Interactions:
Internal – Center for Computational Sciences
External – Ames Laboratory (some nondestructive measurements, powder-metallurgy preparation of ultra-pure samples).

Recognition, Honors and Awards (at least in some part attributable to support under this program):

X.-G. Zhang, Gordon Bell Prize in Computing, 1998.

Personnel Commitments for FY2002 to Nearest +/- 10%:
X.-G. Zhang (30%), W.A. Simpson, Jr. (20%), S.A. David (10%), J. Vitek (10%), and AMES Staff (50%)

Authorized Budget (BA) for FY00, FY01, FY2002:
FY00 BA $350k **FY01 BA $**312k **FY02 BA $**291k

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP and possible subtask under FWP: Radiation Effects

FWP Number: ERKCM04

Program Scope: This program develops mechanistic understanding of the processes by which particle irradiation alters the nano-scale structure, composition and resulting macroscopic properties of materials. Research is carried out to apply this understanding to designing materials for improved performance. Multi-scale theory and modeling, microstructural analyses, and mechanical tests characterize the effort, with theory and modeling closely integrated with experiments

Major Program Achievements (over duration of support): Understood radiation induced swelling on a mechanistic basis, through integration of theory and purpose-designed critical experiments. This work has resulted in proven recommendations for alloy design to reduce or eliminate swelling in applications. Played lead role in developing the theory of irradiation creep. Discovered the new mechanism of gamma-embrittlement of steels in connection with our work to understand the mechanisms of early embrittlement in the HFIR pressure vessel. Applied molecular dynamics simulations to visualize the behavior of high-energy cascades, to determine their efficiency in forming residual defects and clusters, and to determine the effects of pka direction and free surfaces on cascade development. Provided a basic explanation and parameter space mapping for the varying microstructures and modes of deformation in irradiated metals and alloys. Developed a new class of hard surfaced polymers by ion beam treatment, whose surfaces are substantially harder and more wear resistant than steels. Understood the physical bases of these remarkable properties in terms of very high density of crosslinks enabled by the exceptional linear energy transfer of the heavy ions employed.

Program impact: Played a leadership role in the overall development of the field of radiation materials science. Supported the target R&D program for the Spallation Neutron Source by providing the basic underpinning to understand spallation radiation damage and related it to the more well known fission reactor and ion radiation damage. Provided scientific support for applications to predict and improve the behavior of fusion reactor materials and of pressure vessel steels in present day reactors.

Interactions: Forschungszentrum Juelich, Germany; Paul Scherrer Institute, Switzerland; Japan Atomic Energy Research Institute; Electricite de France; Los Alamos National Laboratory; Lawrence Livermore National Laboratory; Department of Nuclear Engineering, North Carolina State University; Materials Science and Engineering Department, University of Tennessee; Materials Department, University of California at Santa Barbara; Department of Nuclear Engineering and Radiological Sciences, University of Michigan

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
K. Farrell, Fellow, Institute of Metals
E. H. Lee, M. B. Lewis, L. K. Mansur, R&D 100 Award for Hard-Surfaced Polymers
E. H. Lee, Scientist of the Year at ORNL
L. K. Mansur, Chairman of Editors, Journal of Nuclear Materials
L. K. Mansur, Fellow, ASM International
L. K. Mansur, Fellow, American Nuclear Society
R. E. Stoller, Fellow, ASTM
Materials Science Competition Awards (two) from DOE-BES

Personnel Commitments for FY2002 to Nearest +/- 10%:
L. K. Mansur (40%), R. E. Stoller (40%), K. Farrell (40%), J. D. Hunn (10%), Postdoctoral Staff (50%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $ 1,319k **FY01 BA $ 632k** **FY02 BA $ 621k**

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP and possible subtask under FWP: High Temperature Alloy Design

FWP Number: ERKCM06

Program Scope: This program focuses on understanding the physical and mechanical metallurgy of ordered intermetallics, with an emphasis on fundamental alloy variables that affect phase stability and mechanical behavior at ambient and elevated temperatures. This understanding will lead to the development of scientific bases for the design of next-generation intermetallic alloys for structural and functional use. Both innovative processing techniques and state-of-the-art microanalytical tools are used for microstructural characterization and control. The observed relationships between mechanical properties and microstructural features are used to model the deformation and fracture of intermetallics. Phase stability, point defects, and magnetic properties are characterized and correlated with site occupation, atomic bonding, and the electronic structure of intermetallics. Recently, efforts have been initiated on understanding physical and mechanical properties of nanophase materials.

Major Program Achievements (over duration of support): Discovered moisture-induced environmental embrittlement at ambient temperatures as a new mechanism responsible for low tensile ductility and poor fracture resistance of many bcc and fcc ordered intermetallics. Understood the ductilizing effect of boron and developed the scientific principles for dramatically improving the ductility of Ni_3Al alloys. Developed a new theory based on thermal vacancies to explain the yield strength anomaly in FeAl alloys. Proposed several dislocation mechanisms to explain deformation twinning in hcp materials and $D0_{19}$ intermetallics. Substantially reduced thermal expansion anisotropy and microcracking in Mo_5Si_3 by quantum mechanical alloy design. Identified magnetic interaction as a new mechanism responsible for unusual solid solution effects observed in NiAl (model alloy). Identified deformation mechanisms in nanocrystalline materials by TEM in situ deformation.

Program impact: This program has provided international leadership in the field of intermetallic alloys through scientific publication and conference organization. ISI has identified two principal investigators, C. T. Liu and E. P. George, among the top 8 most highly cited authors in fields of metallurgy and materials science. The discovery of the mechanism of moisture-induced embrittlement provides new directions for the design of ductile intermetallic alloys. By successfully combining theoretical calculations and experimental studies, this program has demonstrated the potential of designing engineering materials using a quantum-mechanical alloy modeling approach. The discovery of magnetic interaction is expected to provide new insights to explain the unusual solid solution effects in intermetallic and metallic alloys. The scientific principles derived from this BES program help DOE applied programs in the design of ductile and strong intermetallic alloys for engineering use.

Interactions: As a leading intermetallics research group, this task interacts with many universities (including U PA, U TN, U VA, Brown U, Kyoto U, Tohoku U, Beijing U Science & Tech., Ruhr U, and Technical U Chemnitz) and other national laboratories (through CSP Projects) as well as domestic and international materials institutes (IMR and NIMS, Japan) active in intermetallics research.

Recognitions, Honors and Awards: C.T. Liu: Acta Metallurgica Gold Medal Award, 2001, DOE Sustained Outstanding Research Award, 1998, TMS Fellow, 1994, Editor of Intermetallics since 1992; M. H. Yoo: TMS Champion Mathewson Medal Award, 2002, TMS Fellow, 2002; E. P. George: Prof. of U TN, 2002, Humboldt Award, 2000, ASM Fellow, 1999, DOE Sustained Outstanding Research Award, 1998; J. H. Horton: ASM Fellow, 2002.

Personnel Commitments for FY2002 to Nearest +/- 10%: C. T. Liu (50%), M. H. Yoo (100%), E. P. George (40%), J. H. Schneibel (50%), J. A. Horton (40%), L. L. Horton (10%), Z. P. Lu (100%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $ **FY01 BA $** **FY02 BA** $1134k

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP and possible subtask under FWP: Theory and Design of Monolithic and Dual Phase Laves-Phase Alloys

FWP Number: ERKCM30

Program Scope: The objective of this research is to understand the fundamentals of defect structures, phase stability, and deformation mechanisms in Laves phases so that scientific principles can be developed for enhancing their physical and mechanical properties. Initial efforts are devoted to material preparation, microstructural control and defect concentration in monolithic and dual phase materials, and to the study of the deformation and fracture behavior of Laves phase alloys based on Cr_2X-Cr, where X is a refractory metal element, including Nb, Zr, Ta, and Hf. Theoretical calculations are focused on first-principles prediction of electronic structure, defect stability, elastic properties, deformation modes, phase transformation, and the effects of hydrogen absorption.

Major Program Achievements (over duration of support): The study of microstructural features in the Cr-Ta alloy system indicates that the published Cr-Ta phase diagrams and Laves-phase compositions at the eutectic temperature are incorrect. Differences in alloy compositions are detected in C14, C36, and C15 particles in Cr-9.8%Ta, and such differences can be interpreted in terms of the correlation developed based on e/a (number of free electrons per atom). The ternary Cr_2(Nb,Zr) compounds exhibit the C36 crystal structure in the as-cast condition but revert to the C15 structure after annealing. All ΔH values for the binary transition-metal lanthanide Laves phases using the semi-empirical Miedema model were systematically calculated, and these newly calculated data are compared favorably with experimental data. Studies of the structural phase transformation in HfV_2 indicate that its high temperature cubic C15 phase is stabilized by a strong anharmonicity in the shear elastic modulus. First-principles calculations also predict an increased transition temperature for the tetragonal to cubic transformation due to interstitial H in HfV_2. The site preference of hydrogen in ZrX_2 (X=V, Cr, Mn, Fe, Co, Ni) Laves phase compounds was calculated. The site preference of hydrogen is determined by both the interstitial whole size and the electronic states of X atoms.

Program Impact: This program provides the scientific leadership in the study of Laves-phase alloys based on transition metals. The study of microstructures and phase relationships reveals that many published binary phase diagrams for Cr-Cr_2X (X=Nb, Ta, and Zr) are incorrect, and our findings are very usefully for reconstructing these binary phase diagrams. A systematic study of binary and pseudo-binary Laves phase alloys indicates that their fracture toughness at ambient temperatures is not significantly affected by point defect concentration, stacking fault energy, or by the misfit in the coefficients of thermal expansion of Cr and Cr_2X. This is quite contrary to the current thought. An atomistic model is derived to interpret the size-ratio limit for laves phase formation, and this model can be used to ascertain the general trend in the enthalpy of formation in transition-metal Laves phases. The calculations of site preference and local electronic environment of hydrogen will provide new insight for the design of hydrogen storage materials based on Laves phases. The calculations of the intrinsic point defect structure will provide new insight for defect-formation mechanism and phase stability.

Interactions: Maintain close collaborations with Laves-phase research at LANL, University of Pennsylvania, and Brown University. Results of this task provide the scientific principles for improving alloy properties that can be used by DOE applied programs (such as the Fossil AR&TD Materials Program) to develop intermetallic alloys for specific use. Work closely with the S&P Center Project on Design and Synthesis of Ultra-High-Temperature Intermetallics.

Recognitions, Honors and Awards; C.T. Liu: Acta Metallurgica Gold Medal Award, 2001, DOE Sustained Outstanding Research Award, 1998, TMS Fellow,1994, Editor of Intermetallics since 1992; C. L. Fu: TMS Champion Mathewson Award, 2002, DOE Outstanding Accomplishment Award, 1991.

Personnel Commitments for FY2002 to Nearest +/- 10%:
C. T. Liu (10%), C. L. Fu (10%), J. Zhu/Student (30%), M. Krcmar (50%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $151k **FY01 BA $** 143k **FY02 BA** $113k

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0201030

FWP and possible subtask under FWP: Semiconductor Nanocrystals for Carbon Dioxide Fixation

FWP Number: ERKCS41

Program Scope: The combination of atomic resolution Z-contrast scanning transmission electron microscope microscopy, electron energy loss spectroscopy (EELS) and first-principles calculations is used to investigate the catalytic properties of semiconductor nanocrystals for carbon dioxide fixation. Imaging techniques include the determination of atomic structure, three-dimensional reconstruction of nanocrystal shape and spectroscopic identification of surface ligands. First principles techniques are used to investigate nanocrystal nucleation and growth, and catalytic mechanisms of CO_2 fixation.

Major Program Achievements (over duration of support): Image reconstruction techniques have been developed to determine the three-dimensional shape of individual nanocrystals to determine the nature of the exposed facet surfaces on which reactions take place. The goal is to determine the special sites that appear on nanocrystals but are not present on bulk surfaces. EELS is used to investigate the presence of sub-monolayer amounts of oxygen and other impurities on the nanocrystal surfaces. CdS nanocrystals have been chemically synthesized with precise control of crystallite size to allow tuning of electronic properties through quantum confinement effects. Mesoporous SiO_2 and TiO_2 supports have been synthesized and imaged by microscopy. The internal surfaces of the pores have been functionalized and nanocrystals attached.

First-principles theoretical studies have unraveled the detailed mechanisms of the catalytic activity. The key advances in understanding are: 1) the precise role of the nanoscale; 2) that the active site is a surface vacancy; 3) that contrary to previous ideas, the nanocrystal does not catalyze the fixation reactions on its surface, but instead acts as a generator of negatively charged CO_2 molecules which detach from the nanocrystal. These charged molecules are extremely reactive and readily combine with other CO_2 molecules, fixing them as useful organic molecules that could be used as fuels; and 4) that results suggest doped nanocrystals may be effective catalysts in the dark, allowing the development of "artificial leaves" for the removal of CO_2 from the atmosphere.

Program Impact: Publication in Physical Review Letters generated a large number of editorials and write-ups including Scientific American, Physics Today and Materials Today, and websites of American Institute of Physics and American Physical Society.

Interactions: Vanderbilt University, Departments of Physics and Chemistry.

**Recognitions, Honors and Awards (at least partly attributable to support under this FWP

or subtask):

Institute of Physics Thomas Young Medal awarded to S. J. Pennycook and Fellowship of The Institute of Physics. Results are featured in an average of 25 invited talks per year and numerous book chapters

Personnel Commitments for FY2002 to Nearest +/-10%:

S. J. Pennycook (group leader) 40%
A. R. Lupini (post-doc) 20%

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $ 361k **FY01 BA $** 337k **FY02 BA $** 380k

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 03 0

FWP: Domain Structure and Dynamics in Epitaxial Oxides

FWP Number: ERKCM29

Program Scope: From its inception, the broad scope of our research in thin-film oxides has been to study the physics associated with length scale phenomena in ferroelectricity, in particular the fundamental length scales that control phase stability. The overarching goal of this research is to establish a fundamental understanding of the coupling between interfacial electrostatics and microstructure in oxide materials. We are approaching this goal via thin-film studies of crystalline oxides on semiconductors. We rely on and continue to push state-of-the-art ultrahigh vacuum molecular beam epitaxy methodologies in our studies. The research is aimed at developing an atomistic level understanding of the basic forces that control microstructure/property relationships in oxides. A portion of the work described by this FWP is part of the BES Center of Excellence for the Synthesis and Processing of Advanced Materials: "Nanoscale Phenomena In Complex Oxide Thin Films."

Major Program Achievements (over duration of support): Pioneered the field of dielectric physics based on crystalline oxides on semiconductors (COS). Demonstrated ferroelectric polarization reversal in a perfectly commensurate thin-film of $BaTiO_3$ on germanium enabling a two-logic transistor state that offers enormous potential for energy savings in a myriad of electronic sensors and devices.

Program Impact: Research has advanced the development of an atomistic level understanding of the basic forces that control microstructure/property relationships in oxides.

Interactions: As part of Synthesis and Processing Center collaboration, new research collaboration in synchrotron X-ray characterization using standing wave studies to measure the out-of-plane polarization of $BaTiO_3$/Germanium interfaces with Michael Bedzyk at Northwestern University. New nanoscience research collaboration on nanoscale physics initiated with Charles Ahn (Yale University), Karen Rabe (Rutgers University); and Fred Walker (University of Tennessee). A new collaboration between ORNL, Vanderbilt University and Princeton on organic film optics on $BaTiO_3$ on silicon and germanium - (Part of Princeton's NSF Materials Research Science and Engineering Center proposal.) Collaboration with ORNL's (Malcolm Stocks) and NCSU's (Marco Buongiorno Nardelli) theory task is developing the electronic structure characteristics for several oxide/semiconductor systems. Collaborative research is being established with IBM, Zurich and IBM, Yorktown. A Penn State Ph.D. candidate (Curtis Billman) is working at ORNL on BaSrO and strain effects on silicon.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
Rodney McKee: International Advisory Committee, European Materials Research Society, Strasbourg Meeting, June 2003, National Academy of Sciences/National Research Council review panel member of NIST programs, Adjunct Professor at Penn State for thesis supervisory responsibilities, and presented 22 invited talks in major US and European scientific societies (APS, MRS, TMS, ISIF, EMRS and EPS). Established a strong industrial interest in COS with 20 US and Foreign patents and licensing arrangements to exploit a commercial transition of BES fundamental research to industry.

Personnel Commitments for FY2002 to Nearest +/- 10%:
R.A. McKee (80%), F.J. Walker (50%); C.A. Billman (100%)

Authorized Budget (BA) for FY00, FY01, FY2002:
FY00 BA $ 222k **FY01 BA $334**k **FY02 BA $484k**

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0201050

FWP and possible subtask under FWP: FWP Science of Non-equilibrium Processing of Materials

FWP Number: ERKCM05

Program Scope: This program addresses material behavior during non-equilibrium processing, focussing on welding and thermo-mechanical processing. The fundamentals of solidification behavior, correlation of thermal history with phase stability, and mathematical modeling of weld microstructure development are examined. It also seeks to develop a fundamental understanding of materials behavior under non-equilibrium thermo-mechanical processing using coupled multi-length scale modeling of deformation, recrystallization, and grain growth.

Major Program Achievements (over duration of support): Integrated solidification theory with a new geometric model to predict microstructure development in single crystal welds. Identified extreme non-equilibrium solidification behavior during laser welding. Developed a 3-D transient, free-surface, fluid-flow model for predicting weld-pool geometry. Identified and characterized both high-temperature and low-temperature phase stability of austenitic stainless steels and it's influence on impact and creep properties. Developed a coupled thermodynamic and kinetic model for inclusion formation and identified phase evolution during solidification of steel welds using in-situ synchrotron radiation experiments. Developed and applied artificial neural-network models to ferrite number prediction in stainless steels. Organized six International conferences on Trends in Welding Research. Developed fundamental understanding of heterogeneous deformation at the grain level in polycrystalline materials and the formation and evolution of recrystallization nuclei from deformation substructures.

Program Impact: Has advanced the science of non-equilibrium processing and has led to numerous industrial applications and new program development.

Interactions:
Internal—Microscopy and Microanalysis Group, Diffraction and Thermo Physical Properties Group.
External—Pennsylvania State University; Cambridge University, U.K.; Technical University of Graz, Austria; National Institute for Materials Science, Japan; Argonne National Laboratory; Lawrence Livermore National Laboratory; The Computational Materials Science Network (CMSN); Lincoln Electric.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
S.A. David – Editor in Chief- Science and Technology of Welding and Joining, TMS Fellow (2001); Champion H. Mathewson award (2002); Arata Prize (2002); Mckay Helm award (2002); Co-chair International Trends in Welding Research Conference (2002).
J.M. Vitek – Fellow- ASM International; Editorial Board- Science and Technology of Welding and Joining; McKay Helm award (2001); Co-Chair –International Trends in Welding Research Conference 2002.
S.S. Babu—Editorial Board- Science and Technology of Welding and Joining; U-T. Battelle Leadership, Research and Development award; McKay Helm award (2002); Warren F. Savage award (2002).
B. Radhakrishnan—Board of Review Welding Journal; Member of Computational Materials Sciences Network Project (CMSN).
G. Sarma—Member of Computational Materials Sciences Network Project (CMSN).

Personnel Commitments for FY2002 to Nearest +/- 10%:
S.A. David (30%), J.M. Vitek (40%), S.S. Babu (40%), B. Radhakrishnan (30%), G. Sarma (30%), Post doctoral Staff (50%), Technical Support Staff (10%).

Authorized Budget (BA) for FY00, FY01, FY2002:
FY00 BA $722k **FY01 BA $**709k **FY02 BA $**685k

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202010

FWP and possible subtask under FWP:
HFIR Center for Neutron Scattering

FWP Number: ERKCS01

Program Scope: The High-Flux Isotope Reactor (HFIR) is the only high-flux beam reactor operating in the U.S. and one of two worldwide. It is presently undergoing an upgrade to provide larger neutron beams for scattering research and to install a high-performance cold neutron source. This will have a major impact on the neutron scattering capability by providing thermal and cold neutron beams equaled only by the Institut Laue-Langevin in Grenoble, France. In addition to supporting DOE programmatic research, the facilities will be available to the scientific community through an expanded user program. Qualified scientists from academia, industry, and other government laboratories will perform research either independently or in collaboration with ORNL staff. This FWP also includes infrastructure improvements, facility upgrades, and other neutron science support activities.

Major Program Achievements:
In 2001–2002: Determination of magnetic and phonon excitations in superconductors. Discovery of magnetic field-induced antiferromagnetic order in the vortex core of high-T_c superconductors. Measurements of field-induced incommensurate order and gapless excitations in Haldane chains. Exploration of exotic magnetic excitations and field-dependent thermal properties of the quantum magnet $K_2V_3O_8$. Polarized and unpolarized scattering studies of CMR manganites illuminating the magnon-phonon coupling and percolation effects. First observation of microemulsion formation via new anionic phosphate fluorosurfactants, enabling significant water uptake within supercritical CO_2. Demonstration that linear low-density polyethylenes made with next-generation (metallocene) single-site catalysts form a single phase in the melt, as opposed to liquid-liquid phase separation observed in material from traditional multi-site systems. Construction of a conceptual phase diagram for polymer blends, indicating the range of validity of the de Gennes random phase approximation, outside of which molecules contract or expand beyond their unperturbed dimensions, contrary to common assumptions. Demonstration that the concentration fluctuation correlation length collapses onto a master curve for polymers in blends, liquid, and supercritical solvents over a wide range of thermodynamic variables. Determination of the energetics of passage formation in surfactant sponge phases by neutron scattering shear relaxation

Program Impact:
Providing unsurpassed facilities for neutron scattering research. Research using neutron scattering in correlated electron materials, polymers, and soft condensed matter systems. User program for neutron scattering on 15 spectrometers each of which is comparable to the best worldwide.

Interactions
In 2001–2002: Collaborations with 31 universities (including The University of Tennessee, University of California-Santa Barbara, Stanford University, California Institute of Technology, North Carolina State University, Pennsylvania State University, Georgia Institute of Technology, University of Michigan, Lehigh University); 8 national laboratories (including Ames Laboratory, Los Alamos National Laboratory, Brookhaven National Laboratory); and industry (including Advanced Refractories Technologies, Cummins Engine Co., Edison Welding Institute, Pulp and Paper Industry Consortium).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
In 2002: 31 invited talks at national and international meetings, 11 papers published in *Nature*, *Science*, or *Physical Review Letters*. P. D. Butler, Chair, American Crystallographic Association Small-Angle Scattering Interest Group; Co-Chair, First American Conference on Neutron Scattering; Secretary, Spallation Neutron Source and HFIR User's Group; B. C. Chakoumakos,

Chair, Special Interest Group on Neutron Scattering, American Crystallographic Association; Associate Editor for *American Mineralogist;* J. A. Fernandez-Baca co-organizer of CMR Manganites and Related Transition Metal Oxides Workshop, Telluride, Colorado; H. A. Mook co-organizer, APS March Meeting Focus Topic on High Temperature Superconductivity.

Personnel Commitments for FY2002 to Nearest +/-10%:
S. E. Nagler (100%); G. D. Wignall (75%); P. D. Butler (75%); B. C. Chakoumakos (85%); L. Crow (ORNL Postdoc) (75%); P. Dai (100%); J. A. Fernandez-Baca (50%); W. A. Hamilton (50%); M. D. Lumsden (70%); Y. B. Melnichenko (10%); H. A. Mook (75%); L. Porcar (ORNL Postdoc) (100%); J. L. Robertson (50%); S. Spooner (5%); M. Yethiraj (100%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $3,155 **FY01 BA $**3,796 **FY02 BA $**7,359

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202010

FWP and possible subtask under FWP:
Structural Properties of Materials—X-Ray Diffraction

FWP Number: ERKCS09

Program Scope: Fundamental structure and microstructure investigations leading to a basic understanding of the physical properties of technological materials and the development of advanced synthesis and processing techniques; Development and application of high spatially resolved, time-resolved, and momentum-resolved synchrotron x-ray diffraction measurement and analysis techniques, in collaboration with mesoscale dynamics and synthesis of nonequilibrium materials programs, for fundamental investigations of materials microstructure, evolution, and the correlation of microstructure with physical properties of materials; Combined inelastic x-ray scattering measurement and first-principles theoretical calculation investigations of the dynamical electronic response and ectronic correlations in simple and transition metals and transition-metals oxides.

Major Program Achievements (over duration of support):
Development of UNI-CAT general diffraction and inelastic scattering beamline capabilities at the Advanced Photon Source (APS); Development of dedicated micro-diffraction beamline capabilities with two- and three-dimensional x-ray structural microscopy in collaboration with the mesoscale dynamics program; Development of sub-millisecond time-resolved surface-diffraction for real-time, pulsed-deposition thin-film growth investigations and observation of two surface-evolution time-scales in collaboration with synthesis of non-equilibrium materials program; Absolute inelastic x-ray scattering measurements and first-principles dynamical response calculations investigation of frequency and q-dependence of many-body exchange-correlation effects in transition metals; Collaborative structural research leading to the RABiTS approach to fabricating high-J_c superconductors on rolled metal substrates.

Program impact:
Elastic, inelastic, and time-resolved x-ray scattering investigations of the static and dynamic structural aspects of materials and the nature of electronic interactions provide fundamental insight into structure-property relationships in materials of technological importance; Applications of new synchrotron and laboratory based x-ray diffraction techniques supports fundamental investigations of materials growth and processing techniques such as pulsed-laser deposition thin-film growth, novel nanoparticle growth methods, and high-temperature superconductor film fabrication; Inelastic x-ray scattering measurements in collaboration with time-dependent density-functional theory based computations provide a framework for fundamental investigations of many-body exchange-correlation effects in complex metals and metal oxides.

Interactions:
University of Illinois-Materials Research Laboratory; National Institute of Standards and Technology (NIST); UOP Research, Inc.; Howard University; University of TN; Lehigh University; Cornell University; Vanderbilt University; University of California-Santa Barbara; Univ. of Florida; Fisk Univ.; North Carolina State Univ.; University of Alberta (Canada); Magdeburg University (Germany); Energy Efficiency and Renewable Energy Program (Superconductivity Technology Program); ORNL Superconductivity Technology Program.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
RD-100 Award (1999); DOE, Energy 100 Award (2001); American Museum of Science & Energy Tech. Achievement Award (1999); Bertram Warren Diffraction Physics Award (1985); Member, Advanced Photon Source (APS) Users' Organization Steering Committee, (00–03); Member, APS Proposal Review Panel; Member (02–05), APS Beamtime Allocation Committee (02–05); Co-Organizer, Symposium on Nanocrystals, American Physical Society (1998).

Personnel Commitments for FY2002 to Nearest +/- 10%:
J. D. Budai (50%); B. C. Larson (25%); J. Z. Tischler (40%); W. Yang (Postdoc) (50%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $449 **FY01 BA $411** **FY02 BA $503**

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202010

FWP and possible subtask under FWP:
Mesoscale Dynamics and Microstructural Evolution

FWP Number: ERKCS39

Program Scope: The development and application of microbeam x-ray diffraction techniques for fundamental investigations of the microstructure and microstructural evolution of materials on mesoscopic length scales. Research is directed toward building a fundamental understanding of thermal/mechanical/chemical mediated structural evolution, advanced materials synthesis, and advanced materials processing techniques.

Major Program Achievements (over duration of support):
Development of submicron-resolution, white x-ray microbeams; development of the capability for automatic crystal indexing, crystal orientation, and deviatoric/dilatational strain determinations in 2-dimensions with submicron resolution. Development of 3-dimensional (3D) x-ray structural microscopy capabilities, including point-to-point crystal structure, orientation, and strain with submicron resolution. Nondestructive, 3D measurement of structure, orientation, size, and morphology of individual grains in polycrystalline Al, elastic strain tensors and plastic deformation/microstructure in deformed materials with submicron resolution over mesoscopic length scales.

Program impact:
A new x-ray structural microscopy has been established with submicron resolution in 2D and 3D using x-ray microbeams that is applicable to single-crystal, polycrystalline, composite, functionally-graded, and deformed materials. The capability provides a direct link between the structure and evolution of materials and large-scale computer simulations and multi-scale modeling on mesoscopic length scales of tenths of microns to hundreds of microns.

Interactions:
Materials Research Laboratory at the University of Illinois, Urbana-Champaign; Los Alamos National Laboratory, Sandia National Laboratories, Pacific Northwest National Laboratory, the National Institute for Standards and Technology, Alcoa Technical Center, Ohio State University, University of Tennessee and Magdeburg University (Germany) on fundamental aspects of deformation on mesoscopic length scales in polycrystallinemetals and ceramics; Lehigh University, IBM, and Sandia National Laboratory on strain in metal interconnects and metal overlayer induced strain in Si; University of California-Santa Barbara and Vanderbilt University on mesoscale dynamics theory and materials evolution; State University of New York, Stony Brook, on crystal structure and defects in single crystals formed by nanoballs; Harwell Laboratory (UK) on biological applications of 3D x-ray structural microscopy; Ford Motor Company, NASA, and an Industrial Whiskers Fundamental Taskforce to measure local texture, strain and deformation in critical materials systems; and experimental and computational materials programs within ORNL. Ongoing interactions exist with the European Synchrotron Research Facility (ESRF), the Advanced Light Source (ALS), the Swiss Light Source, the National Synchrotron Light Source (NSLS), the Taiwan Light Source, the Canadian Light Source, the Australian Light Source, the Ukrainian Light Source, the Korean Light Source (Pohang), CHESS, and the Advanced Photon Source.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask:

R&D 100 Award for "Differentially Deposited X-Ray Microfocusing Mirrors" (2000); Semi-Finalist Discover Award for "3D X-Ray Crystal Microscope" (1999); 25 invited talks 2000–2002.

Personnel Commitments for FY2002 to Nearest +/- 10%:
G. E. Ice (40%); J. D. Budai (30%); B. C. Larson (25%); J. Z. Tischler (25%); W. Liu (Postdoc) (100%); W. Yang (ORNL) (50%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $700 **FY01 BA $**643 **FY02 BA $**982

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0202010

FWP and possible subtask under FWP: X-ray Research Using Synchrotron Radiation

FWP Number: ERKCM02

Program Scope: Development and application of advanced x-ray techniques that exploit ultra-brilliant synchrotrons to study materials, with an emphasis on understanding the role of local correlations on materials properties.

Major Program Achievements (over duration of support):
Pioneered x-ray focusing/monochromating optics including graphite monochromators, dynamically bent sagittal-focusing crystals and differentially deposited Kirkpatrick-Baez microfocusing mirrors.

Discovered the Resonant-Raman X-ray and Resonant-Raman Auger effects.

Pioneered synchrotron fluorescence microprobe measurements of trace elements. Pioneered numerous x-ray techniques including synchrotron fluorescence microprobe, multi-wavelength holography, resonant magnetic scattering, diffraction anomalous fine-structure measurements of interface chemistry/structure and more.

Developed the Borie-Sparks and 3λ methods to interpret local correlations from diffuse x-ray scattering measurements. These methods are used world wide to interpret the near-neighbor correlations in solid-solution alloys. Showed how the 3λ method could be used to provide information with unprecedented accuracy about the average near-neighbor bond distances in solid solution alloys. Demonstrated that magnetic annealing causes anisotropic chemical ordering in Ni-Fe alloys. Demonstrated chemically specific bonding in Ni-Fe alloys that challenges traditional models of alloy structure.

Developed models for percolative current transport in high-temperature superconductors that explain local x-ray texture measurements and conductivity results.

Program impact: X-ray optics and advanced x-ray techniques and theories are used worldwide to study materials. Measurements of local correlation are guiding emerging theories of alloy structure.

Improved understanding of the effect of crystallographic texture on superconducting properties is leading to the development of a new generation of superconducting wire.

Interactions: Collaborations with scientists from University of Tennessee Knoxville, Boston University, University of Houston, U. of Illinois Urbana/Champaign, U. of Munich, KFA Julich, ETH Zurich, CECM, U. of Grenoble, the Institute of Metal Physics Kiev, Pohang South Korea, ESRF, APS, ALS, SSRL.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): ORNL Scientific Research Team of 2002; R&D 100 Award for "Differentially Deposited X-ray Microfocusing Mirrors" (2000); Semi-Finalist Discover Award for "3D X-ray Crystal Microscope" (1999); 2Fellows American Physical Society; R&D 100 Award for RABiTS (1997), BES Maerials Sciences Research Award in Solid State Physics (1996), DOE Sustained Outstanding Achievement Award: Metals and Ceramics 1991; MMES Achievement/Publication Awards 1986,1992, 1995, 1997, 1998, 1999; IR-100 Award for Development of X-ray Monochromator 1983; U.S. Patent for Sagittal Focusing X-ray Monochromator 1983; 27 Invited talks in FY2000 and FY2001.

Personnel Commitments for FY2002 to Nearest +/- 10%:
Gene Ice (group leader)30%, Eliot Specht (30%), Cullie Sparks(60%), Rosaliya Barabash (100%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $479k **FY01 BA** $437k **FY02 BA** $402k

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202020

FWP and possible subtask under FWP:
Thin Film and Nanostructured Materials Physics

FWP Number: ERKCS04

Program Scope: Fundamental studies of film-growth mechanisms, thin-film properties, and the growth environment are carried out to create multilayered or nanostructured materials with new or enhanced properties. Experiments focus on energetic beam-assisted growth methods to control composition and nanostructure; time-resolved, in situ monitoring to understand growth mechanisms and optimize growth processes; and the use of artificial heterostructures to control optical, electrical and mechanical properties. Nanosecond time- and spatially resolved gated imaging and optical spectroscopy techniques are developed and used to identify incident species and their kinetic energies, and to determine timescales and optimal conditions for growth. Sophisticated ellipsometry and related optical methods are developed for nondestructive evaluation of films, multilayers, and interfaces.

Major Program Achievements (over duration of support):
(1) Discoveries and understanding of the growth mechanisms of vertically aligned carbon nanofibers, including shape control via their relative longitudinal and transverse growth rates; demonstration that the transition between growth "from the tip" and "from the base" can be kinetically controlled; and derivation of a model that explains why vertical alignment occurs only if the catalyst nanoparticle is located at the growing tip (not the base). (2) Discovery with ORNL collaborators of nanoscale "superionic" conductivity in pulsed-laser deposited ZrO_2-10 mol% Y_2O_3 films for film thicknesses <50 nm, resulting in a more than 100-fold increase of ionic conductivity in comparison with the bulk material. (3) Discovery that high-yield laser vaporization growth of single wall carbon nanotubes (SWCNTs) occurs by the condensed phase conversion of carbonaceous clusters and nanoparticles, and can be re-started ex situ. (4) The first growth of high-J_c (>500 kA/cm^2) YBCO films on non-magnetic rolling-assisted biaxially textured substrates (RABiTS). (5) The first direct epitaxial growth of Si and Ge nanostructures on locally e-beam patterned hydrogen-terminated Si surfaces.

Program impact:
(1) Leaders internationally in the use of time-resolved in situ electrical, spectroscopic, and imaging techniques to determine the time evolution of species in the plasma "plume" used for pulsed-laser deposition (PLD). These data have enabled understanding the time evolution of precursor species responsible for the growth of SWCNTs by laser vaporization, for PLD of numerous metal oxide films, and the first description of heavy biomolecule propagation during laser desorption of organic crystal matrices. (2) Completely deterministic (patterned) growth of vertically aligned carbon nanofibers, resulting in precise sub-micrometer positioning of nanofiber arrays, and enabling demonstrations of their use as field-emitting cathodes in nanoelectronic devices and for gene transfer and electrochemical probing of living cells. (3) World-leading capabilities for the detection of anisotropy in optical materials, through development of two-modulator generalized ellipsometry (patented by ORNL). (4) Commercial development of RABiTS for practical high-temperature superconductors.

Interactions:
External (2002)—Collaborations with 11 universities (including UC-Berkeley, Cornell, Florida, Imperial College (UK), Michigan, Tennessee, and Vanderbilt), 7 industries (including Hinds Instruments CRADA, Motorola, Neocera, and SEMATECH), and 5 government research labs (including Argonne NL, Lawrence Berkeley NL, NASA Langley, and NASA Marshall).
Internal (2002)—Extensive collaborations on laser ablation growth of HTSc on metal foils (DOE EE/RE) and with Metals and Ceramics, Chemical Sciences and Life Sciences Divisions.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
(2001–2002 only) 13 invited talks at national / international conferences. Organizers of two APS, one MRS, and one SPIE symposium, and memberships on program committees for four national and international conferences.

Personnel Commitments for FY2002 to Nearest +/- 10%:

D. H. Lowndes (group leader) 20%; G. Eres 20%; D. B. Geohegan 20%; G. E. Jellison 20%; H.-M. Christen 20%; C. M. Rouleau 20%; A. A. Puretzky (guest scientist) 50%; H. Cui (ORNL postdoc) 20%

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$869,000 **FY01 BA** \$740,000 **FY02 BA** \$716,000

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202020

FWP and possible subtask under FWP:
Synthesis and Properties of Novel Materials

FWP Number: ERKCS06

Program Scope: Significant fundamental and applied research problems in the fields of solid state physics and materials science are addressed through the application of modern methods and techniques for the modification, synthesis, crystal growth, and characterization of advanced materials. Supporting DOE programs and technologies through increasing our understanding of the fundamentals of matter plus enhancing U.S. competitiveness and homeland security represent the overall objectives of this effort

Major Program Achievements (over duration of support):
Discovered a new vacuum ultraviolet (VUV) scintillator for use with proportional counters for x-ray and gamma-ray detection. Discovered a new family of long-wavelength scintillators for use with solid state detectors. Discovered and developed a new family of high durability, radiation resistant glasses for optical and waste disposal applications. Made the first observation of size effects in nanoparticles of metal-insulator transition materials and modeled this phenomenon. Developed a new family of "smart" near-surface nanocomposite materials. Made the first observation of a size dependence in the crystalline-to-amorphous phase transition of nanocrystalline solids. Discovered the ability to produce large increases in the coercive field of magnetic nanoparticles by heavy-particle bombardment and thereby reduce superparamagnetic effects. Delineated the mechanisms for the formation of hollow nanoparticles and void structures in nanophase materials. Discovered and modeled a temperature-controlled surface plasmon resonance effect in nanophase particles of the metal-insulator-transition material VO_2 formed in an amorphous SiO_2 host.

Program Impact:
The activities of this effort continue to impact a wide range of DOE programs that range from nuclear non-proliferation to environmental remediation to nuclear waste disposal. The effort has attracted a significant and continuing level of non-BES research support from other DOE programs.

Interactions:
Harvard Univ., Vanderbilt Univ. Cambridge Univ, Univ. of Michigan, Univ. of California-Davis, Florida Univ., Florida State Univ., Tulane Univ., Univ. of Kentucky, Univ. of Tennessee, Baylor Univ., ANL. PNNL, LBL, Univ. of Alberta (Canada).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
L. A. Boatner: Frank H. Spedding Award for Excellence in Rare Earth Research (2002); Jesse W. Beams Prize of the American Physical Society Southeastern Section (2001); Elegant Work Prize of the Institute of Materials of the United Kingdom (1997); Federal Laboratory Consortium Award for Excellence in Technology Transfer (1997); The Francis F. Lucas Award of the American Society for Metals International (1988); The Pierre Jacquet Gold Medal Award of the International Metallographic Society (1988); R&D–100 Award Winner (1996, 1988, 1982); Significant Implications for Energy Technology in Solid State Physics Award, 1984; DOE Materials Sciences Research Competition; Oxford Cryosystem Award for Low-Temperature Analysis [presented by the American Crystallographic Association (2001)]; Corresponding Member of the Academia Mexicana de Ciencias [Academy of Sciences of Mexico (1997)]; Science Digest–100 Most Significant Technological Achievements in 1984–1985: Member of the Editorial Board of Applied Physics Reviews (2001–present); Chair, Committee on International Scientific Affairs, The American Physical Society (1999); Review Editor, *The Journal of Materials Research* (1995–2002).

Personnel Commitments for FY2002 to Nearest +/- 10%:
L. A. Boatner (50%), J. O. Ramey (25%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $748	**FY01 BA $**685	**FY02 BA $**355

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202020

FWP and possible subtask under FWP:
Synthesis and Properties of Superconductors

FWP Number: ERKCS15

Program Scope: Synthesis, characterization, and optimization of high-temperature superconductors (HTSc) and related materials for a basic understanding that contributes to the development of practical devices. Emphasis is placed on the production of controlled defect structures for improved flux pinning and critical currents; understanding and overcoming the fundamental current barriers posed by grain boundaries in HTSc; the development of chemical and structural compatibility of thick, high-current HTSc coatings with metal tape substrates; and the influence of anisotropic material properties on fundamental electronic characteristics and superconducting parameters.

Major Program Achievements (over duration of support):
Related meta-stabilities in the structural properties of the vortex lattice (by neutron scattering) with history-dependent flux pinning and critical currents. Assessed the impact of randomly oriented columnar defects on the *equilibrium* magnetization of HTSc materials in the regime of strong thermal activation. Gained understanding and control of the epitaxial deposition of oxides on metal surfaces of nickel, nickel alloys, and copper, including progress toward the development of a single, rather than multiple stack, buffer layers. Elucidated the current-limiting nature of small-angle grain boundaries in YBCO. Developed process optimization of thick YBCO films needed for the ultimate development of high-current HTSc coated conductors. Evaluated the potential of emerging materials, including investigations of the newly discovered superconducting compound MgB_2, where the important effects of material anisotropy and nanoscale defects have been assessed.

Program Impact:
Provided a scientific basis for understanding and controlling the epitaxial deposition of oxides on metal surfaces of nickel, nickel alloys, and copper, and has progressed toward the development of thick HTSc coatings that have large critical current densities.

Interactions:
Internal: Metals and Ceramics Division; Chemical Sciences Division; Electron Microscopy, Neutron Spectrometry, Thin Films and Nanostructured Materials, Ion-Solid Interactions, X-Ray Diffraction
External: Argonne National Laboratory; Los Alamos National Laboratory; University of Wisconsin; University of Kansas; University of Florida; University of Barcelona

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
D. K. Christen: 2001 Co-Recipient, DOE/EERE Office of Power Technologies Research Partnerships Award; 2001 Co-Recipient, Federal Laboratory Consortium Award of Excellence in Technology Transfer; Co-Organizer, DOE Superconducting Wire Workshop, St. Petersburg, Florida, January 2002; Co-Organizer, Applied Superconductivity Conference, Houston, Texas, August 2002.
R. Feenstra: 2001 Co-Recipient, DOE/EERE Office of Power Technologies Research Partnerships Award; 2001 Co-Recipient, Federal Laboratory Consortium Award of Excellence in Technology Transfer; Co-Organizer, MRS Fall Meeting, Symposium E, Boston, MA November, 2001; Co-Organizer, MRS International Workshop on Processing and Applications of Superconductors, Gatlinburg, Tennessee, August 2002; MRS Fall Meeting, Symposium S, Boston, Massachusetts, December 2002.

Personnel Commitments for FY2002 to Nearest +/- 10%:
D. K. Christen (10%), R. Feenstra (10%), H. R. Kerchner (100%), D. H. Lowndes (10%), J. R. Thompson (50%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA \$850k **FY01 BA** \$770 **FY02 BA** \$457

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202020

FWP and possible subtask under FWP:
Electron Microscopy of Materials

FWP Number: ERKCS18

Program Scope: The techniques of atomic-resolution *Z*-contrast scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) are developed to enable determination of local atomic and electronic structure at interfaces and nanostructures. Aberration correction is being applied to take these techniques into the sub-Ångstrom regime with unprecedented improvements in sensitivity, including the capability for imaging, lattice location and spectroscopy of individual atoms within materials and on their surfaces. Theory is used to investigate the fundamental quantum mechanical limits to resolution, which are anticipated to be reached in the near future. Theory is also used to invert spectroscopic data for the determination of local valence and electronic structure.

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Major Program Achievements (over duration of support):
Over the last 15 years, the Electron Microscopy Group has played a pioneering role in the development of atomic-resolution imaging and spectroscopy with the STEM. In 1988, we were the first group to claim, against prevailing wisdom, that crystal images obtained with a high-angle annular detector were in fact incoherent images, able to be reveal the location of each atomic column, the brightness of which reflected its atomic number, *Z*. We claimed such *Z*-contrast images to be directly interpretable, unlike conventional images. A Bloch wave analysis unraveled the quantum mechanical explanation for this behavior, and results were published in *Nature* and *Physical Review Letters*. This overall physical picture remains accurate today. In 1993, we were the first group to demonstrate atomic resolution electron energy loss spectroscopy, which appeared in *Nature*. All these results were obtained with a 100-kV STEM; and in 1995, we took delivery of a 300-kV STEM, with a 0.13-nm beam and demonstrated resolution of the Si dumbbell, a landmark achievement at that time. This machine produced the world's smallest beam, and in 1998 was the first to achieve sub-Ångstrom resolution, 0.078 nm. It was the first commercial STEM to reveal atomic configurations of ultra-dispersed catalyst clusters without the need for specialized support films. These results appeared in *Science* and *Physical Review Letters*, and new insights were obtained into dislocation core structures at interfaces and grain boundaries, nanotubes, nanocrystals, quasicrystals and superlattices. In 2002, an aberration corrector was installed on this microscope which has generated a 0.05-nm beam, a new world record.

Program Impact:
Program has contributed to the commercial development of atomic-resolution STEM and the explosion in purchases in the U.S. and worldwide. Instruments are now available from two major overseas companies and a U.S. startup company. Program has contributed to 6 articles in *Nature* or *Science*, 25 *Physical Review Letters*, 13 book chapters and 4 encyclopedia articles.

Interactions:
Vanderbilt University, North Carolina State University, University of Illinois at Chicago, University of Cambridge, Northwestern University, University of Florida, University of Pennsylvania, National Institute for Materials Research, Japan, Dartmouth College, Massachusetts Institute of Technology.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
S. J. Pennycook: Materials Research Society Medal, Institute of Physics Thomas Young Medal, and Fellowship of the Institute of Physics and the American Institute of Physics. Results are featured in an average of 25 invited talks per year.

Personnel Commitments for FY2002 to Nearest +/-10%:
S. J. Pennycook (Group Leader) 25%; M. F. Chisholm 25%; A. Lupini (postdocs)33%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $700,000 **FY01 BA** $630,000 **FY02 BA** $603,000

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202020

FWP and possible subtask under FWP:
Synthesis of Nonequilibrium Materials and Structures Using Laser-MBE

FWP Number: ERKCS32

Program Scope: Fundamental research is carried out to obtain a detailed understanding of nonequilibrium growth of crystalline thin films using pulsed, energetic ablation beams under reactive growth environments. Pulsed-laser ablation (PLA) is combined with in situ, time-resolved synchrotron x-ray surface-diffraction measurements at the Advanced Photon Source (APS), in order to probe separately the initial crystallization stage and subsequent near-surface evolution. Simulation and kinetic modeling are employed to understand and control growth kinetics. These methods permit real-time, in situ investigation of heteroepitaxial thin-film growth commensuration/discommen-suration processes. Parallel laser-MBE film-growth experiments at ORNL are used to select growth regimes for detailed study at the APS, and to investigate effects of pulsed delivery of ambient gases before, during, or after the ablation pulse. World-leading capabilities for two-modulator generalized ellipsometry (patented by ORNL) are used with scanning probe microscopy to compare films and interfacial layers grown at the APS and ORNL.

Major Program Achievements (over duration of support):
Direct observation that the crystallization and surface-evolution phases of PLA film growth can occur on widely separated time-scales (milliseconds vs seconds). Use of simultaneous specular (0 0 1/2) and non-specular (0 1 1/2) surface truncation rod scattering to monitor in-plane and surface-normal lattice registry during real-time studies of layer-filling and defect formation, for homoepitaxial PLA growth of $SrTiO_3$. Use of surface truncation rod diffuse scattering to monitor island size as a function of layer coverage, during PLA growth of $SrTiO_3$. Multi-layer modeling of homoepitaxial $SrTiO_3$ film-growth, showing that $SrTiO_3$ behaves like a nearly ideal two-layer system, with essentially unimpeded interlayer mass transport between 550 and 650^{o} C. Direct observation of lattice strain-relief discommensuration during formation of the first two crystalline layers, for heteroepitaxial PLA of ZnO on Al_2O_3. Demonstration that kinematical x-ray scattering permits testing time-domain film-growth models and provides information beyond that derived from RHEED measurements.

Program impact:
Information needed to understand the evolution of crystalline thin films is available through detailed analyses of the surface-sensitive truncation rods and truncation-rod diffuse x-ray scattering. Using these methods, this program has produced the first detailed information about the time scales and surface structures associated with crystallization and aggregation processes, separated from observations of subsequent surface evolution through interlayer transport. The information generated regarding the growth of complex oxide materials that have both fundamental and technological importance will provide a basis for formulating the science of nonequilibrium growth of phases that are not accessible by equilibrium growth methods. The quantitative analyses developed in this program will provide a basis for modeling PLA thin-film growth, and will increasingly be directed toward developing new regimes of materials synthesis in terms of speed, structure control, and film perfection.

Interactions:
Choices of materials for study at the APS are influenced by the needs of other ORNL programs that focus on understanding highly electronically correlated transition metal oxides. Thin-film optical measurements are carried out in collaboration with four industries including Motorola and SEMATECH; with the Max Planck Institute (Halle, Germany); and, with six universities including Cornell, Florida, Michigan, and Vanderbilt.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): Approximately 10 invited talks at national and international conferences and workshops; two invited book chapters; organizers of two APS focused sessions; memberships on program committees of national and international conferences. B. C. Larson: Chair, Program and Advisory Board, Cornell High Energy Synchrotron Source. J. D. Budai: Member, APS Users Organization Steering Committee (UOSC). J. Z. Tischler: Past Chair, APS UOSC.

Personnel Commitments for FY2002 to Nearest +/- 10%:

D. H. Lowndes (10%); B. C. Larson (25%); J. Z. Tischler (25%); J. D. Budai (15%); G. Eres (40%); C. M. Rouleau (20%); G. E. Jellison (10%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$480 **FY01 BA** \$420 **FY02 BA** \$386

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202020

FWP and possible subtask under FWP:
Center for Nanophase Materials Sciences

FWP Number: ERKCS48

Program Scope: The Center for Nanophase Materials Sciences (CNMS) is a multidisciplinary nanoscience user research center being developed by ORNL in partnership with the scientific community. Its research will be organized under three scientific thrusts: soft materials, complex hard materials, and theory / modeling / simulation. Distributed over these thrusts will be approximately 10 research focus areas, selected with the scientific community and approved by the Center's Scientific Advisory Committee. The CNMS will occupy approximately 80,000 sf in a new four-level building that contains wet and dry research laboratories, a Nanomaterials Theory Institute, conference rooms and office space for 190 staff members and visitors, and an adjoining single-level Nanofabrication Research Laboratory equipped with clean rooms and support spaces for nanofabrication, soft-hard materials integration, and nanoscale imaging and manipulation. The CNMS will include specialized equipment needed to synthesize nanomaterials, to monitor their growth, and for complementary structural, chemical and properties characterizations.

Major Program Achievements (over duration of support):
The purpose of this FWP is to fund other project costs associated with acquisition of the CNMS building, the definition of associated technical equipment needs, and assessments of proposed operations. Two Planning Workshops were held (October 2001 and June 2002) in order to build research community consensus regarding the greatest scientific challenges and technological opportunities that the CNMS should address, the desired mode of operation, and related infrastructure needs. The CNMS had its DOE Conceptual Design Review in December 2001, an External Independent Review in July 2002, and design of the building was completed in November 2002. Following a DOE Independent Project Review in December 2002, construction is expected to begin in April 2003 and to be completed in November 2004, followed by a phased occupancy beginning in December 2004, with full operation scheduled for 2006.

Program impact:
The CNMS will integrate nanoscale science with neutron science, synthesis science, and with theory / modeling / simulation, synergistically bringing together four areas in which the United States has clear national research needs. The CNMS will be located on ORNL's new Spallation Neutron Source campus, thereby providing easy access to world-leading expertise and facilities for neutron scattering studies of nanoscale materials and phenomena. Expanding upon the tradition of DOE user research centers, it is expected that a significant fraction of the long-term researchers at the CNMS will be from outside ORNL, with numerous additional graduate students, postdoctoral scholars and short-term visitors. In addition to its research mission, the CNMS will provide a fertile training opportunity for students and researchers new to advanced synthesis techniques, nanomaterials modeling, neutron characterization and multidisciplinary research.

Interactions:
The CNMS is part of a national DOE user network of five Nanoscale Science Research Centers (NSRCs). It is closely integrated with the other four NSRCs through a shared gateway website, common provisions for user access, reciprocal workshops, and a joint national user meeting. The CNMS also builds upon current BES-funded materials and chemical sciences research programs, with neutron characterization at the SNS and the newly upgraded High Flux Isotope Reactor (HFIR) as a critical element. The CNMS does not duplicate equipment or expertise available at other ORNL user or collaborative research facilities, but instead will leverage their use for nanoscience research. In addition, the CNMS will collaborate with other regional (often university-based) and national nanoscience R&D efforts through its short-term visitors, long-term staffing, and joint postdoctoral programs.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
None

Personnel Commitments for FY2002 to Nearest +/- 10%:
None

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $0 **FY01 BA** $250,000 **FY02 BA** $225,000

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202020

FWP and possible subtask under FWP:
The Emergence of Nanoscale Cooperative Phenomena: Fundamental Studies Using Self-Organized and Artificially Structured Materials **Subtask:** Single Crystal Nanotubes

FWP Number: ERKCS49

Program Scope: This FWP focuses on highly correlated electronic behavior in transition metal oxides (TMOs) that results in their astonishing range of properties, exemplified by high-temperature superconductivity and colossal magnetoresistance. The objective is to understand and learn to control TMO properties by growing artificially structured materials in which dimensional confinement, strain, or the interaction with an adjacent nanoscale phase across an interface are used to select among competing states (phases). This is accomplished by synthesizing artificial materials with variable dimensionality, e.g. 3D→2D (in layered materials and superlattices) and in "1+"D (coupled quantum nanowires). The materials used include magnetic and ferroelectric oxides as well as Bi- and Cr-based multiferroics. Strong theoretical support is provided by ORNL and external collaborators and a Summer Theory Workshop with leading TMO theorists, graduate students and postdoctoral scholars. **Subtask:** ORNL and Rice University perform fundamental studies of single-wall carbon nanotube (SWCNT) growth, focused on methods to (i) control SWCNT diameter and chirality and (ii) align and assemble SWCNT into crystalline structures.

Major Program Achievements (2001–2002):
(1) Development of a new Continuous Compositional Spread combinatorial synthesis method to rapidly and efficiently search the large space of metastable (mainly high-temperature) TMO phases and enable their use in superlattice structures. (2) Joint theoretical-experimental collaboration demonstrating fabrication of magnetic dot arrays with narrow size distributions on an insulating substrate, driven by strain-mediated dot-dot interactions. **Subtask:** Direct demonstration that the 2001 report in Science (by Cambridge and IBM Zurich groups) of the growth of "faceted nanoscale crystals of aligned SWCNTs" is not correct, together with the correct identification of similar faceted crystals grown at high temperatures at ORNL as calcium-intercalated molybdenum oxide.

Program impact:
This research addresses the dominant scientific theme of our time, the fundamental and practical importance of understanding complex, self-organizing nanoscale behavior. The practical objective is to understand and control the results of coupling dissimilar ordered phases by placing them in close proximity on the nanoscale, thereby creating enhanced or entirely new combinations of properties. The experimental results provide important data for a collaborating group of leading theorists. **Subtask:** Aligned and close-packed SWCNTs of the same chirality are predicted to have extraordinary multifunctional properties for energy applications: light weight combined with exceptional thermal conductivity, strength and electrical conductivity. The research develops methods that potentially offer rapid growth rates for such materials.

Interactions:
Development of a broad, interactive theory program through collaborations with leading theorists at Natl. High Magnetic Field Lab./Florida State, Cincinnati, Rutgers, Yale, Natl. Inst. of Adv. Industrial Science and Technol. (Japan) and Inter. Ctr. for Quantum Structures (Beijing), and by establishing a Summer Theory Workshop program associated with this FWP. Other collaborations with universities of Alabama, Florida, Texas-Austin, Joint Res. Ctr. for Atom Technol. (Japan), Lawrence Berkeley NL, NASA Langley, NASA Marshall, and Neocera, Inc.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
(2001–2002 only) Approximately 25 invited talks at national / international conferences; Welch Award and Fellowship in the AVS (E. W. Plummer); Director, Ctr. for Nanophase Materials Sciences (D. H. Lowndes); extensive activity by program personnel organizing APS focused sessions, MRS symposia, SPIE symposia, and international conferences and workshops.

Personnel Commitments for FY2002 to Nearest +/- 10%:

H. M. Christen (50%); S. Dai (35%); G. Eres (20%); D. B. Geohegan (50%); D. H. Lowndes (30%); D. G. Mandrus (30%); E. W. Plummer (10%); A. A. Puretzky (guest scientist, 50%); T. C. Schulthess (50%); J. Shen (30%); Z. Zhang (25%); 4 ORNL postdoctoral scholars (100% each) ; M. F. Chisholm (collaborator) ; P. Dai (collaborator); S. Nagler (collaborator); S. J. Pennycook (collaborator).

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA \$0 **FY01 BA** \$1,300,000 **FY02 BA** \$1,520,000

Laboratory Name: Oak Ridge National Laboratory **B&R Code:** KC0202020

FWP and possible subtask under FWP:
Low Dimensional Materials by Design

FWP Number: ERKCS52 (replaces ERKCS11 and part of ERKCS40)

Program Scope: The focus of this task is the science-driven synthesis of artificially structured materials with novel behavior in constrained dimensionality. This program revolves around a multitude of advanced growth and nanoscale characterization techniques coupled closely to modeling and theoretical predictions. Materials receiving the greatest attention are those with novel magnetic or electronic properties such as transition metal oxides. A key strength of the program lies in the in situ coupling of an array of non-equilibrium growth and fabrication techniques with a large ensemble of nanoscale characterization techniques (magnetic, electronic, and structural). Current synthesis capabilities include molecular beam epitaxy (MBE), pulsed laser MBE, and direct writing with a scanning probe, with new capabilities to be developed as needed. In situ characterization capabilities include ultra-high vacuum scanning tunneling microscopy (STM), atomic force microscopy, electron diffraction and magneto optical (linear and nonlinear) Kerr effect. Anticipated accomplishments, in collaboration with theorists at ORNL, are the discovery of novel physical properties and emergence of new concepts that result from low dimensional confinement.

Major Program Achievements (over duration of support):
Identification of a magnetic capping layer induced spin reorientation phase transition in ultrathin films; observation of intertwining of charge density waves (CDW) and defect-ordering phase transitions in 2-D systems [Sn/Ge(111)]; first measurement of the anisotropic conductivity along and across nanowires of Ga on Si(112); determination of compressive stripe phase growth in a thin film of Ag on Ru(0001); studied the role of surface structure and chemistry on epitaxial seed layer growth of superconducting thin films on rolling assisted biaxially textured Ni(001); determination of surface nanocluster decay and reshaping mechanisms on Cu surfaces; determination of a compressive stripe phase in growth of thin films of Ag on Ru(0001); obtained the pure magnetic phase diagram of fcc Fe/Cu(100) ultrathin films by eliminating the influence of structural changes; explored the nature of melting of the magnetic stripe phase in the Fe/Cu(100) system.

Program Impact:
Has developed novel growth techniques and combined them with in situ analysis techniques to characterize magnetic, electrical transport, and morphological properties of low dimensional nanostructures.

Interactions:
The University of Tennessee (UT) and the University of Texas–Austin: thin-film growth; CAMD and Louisiana State University: metallic alloy surfaces and thermal expansion; Max-Planck-Institut für Mikrostrukturphysik: thin-film and surface magnetism; BNL and Sandia National Laboratory, Albuquerque: x-ray scattering studies of dislocations at surfaces and interfaces; Iowa State University and National Taiwan University: nanocluster shape evolution on surfaces; Exchange program with the Center for Quantum Structure China (Chinese Academy of Sciences) in Beijing; California State University: spin engineering in magnetic ultrathin films; Argonne National Laboratory: beam line ID9 at the APS.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Medard W. Welch Award, 2001, awarded to E. W. Plummer; Fellowship in the American Vacuum Society, awarded 2001 to J. F. Wendelken and E. W. Plummer; ORNL Wigner Fellows, J. Shen and L. Petersen; Fowler-Marion Outstanding Graduate Student Award from the University of Tennessee awarded to J. Pierce; ORNL/UT Distinguished Scientist, E. W. Plummer. Patent awarded for a method for self-organized fabrication of quantum dots, J. F. Wendelken with Z. Zhang. 17 invited talks.

Personnel Commitments for FY2002 to Nearest +/- 10%:
A. P. Baddorf (70%); Z. Gai (visiting scientist) (40%); G. Farnan (postdoc) (40%); E. W. Plummer (Distinguished Scientist) (20%); J. Shen (70%); J. F. Wendelken (90%); H. Weitering (joint U. of Tennessee faculty) (30%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $840 **FY01 BA $**765 **FY02 BA $**1,067

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202020

FWP and possible subtask under FWP:
Correlated Electron Materials

FWP Number: ERKCS53 (replaces part of ERKCS06 and part of ERKCS40)

Program Scope: The Correlated Electron Materials (CEM) Group applies the experimental tools of materials synthesis, compositional tuning, and crystal growth to address cutting-edge issues in condensed matter physics. A large fraction of the group's effort is devoted to the development of new materials with intriguing physical properties. A smaller, but still significant fraction of the group's effort is devoted to the preparation of high-quality single crystals for in-depth experiments. The basic physical properties of materials are determined within the CEM Group. Measurements of electrical and thermal transport, heat capacity, magnetization, and structure are routinely performed. Members of the CEM Group are regular users of the NHMFL, the HFIR, the NCNR, and the NSLS. An important dimension of the CEM Group's scientific impact is to suggest experiments and provide samples to an ever-widening circle of collaborators.

A major focus of the CEM Group's research involves the study of novel cooperative phenomena, nanoscale electronic phase separation, and quantum criticality in transition metal oxides. Other focal areas include thermal transport and neutron scattering on electron-doped high-T_c superconductors, development of new (bulk) dilute magnetic semiconductors, and the design and synthesis of novel low-dimensional and molecular-scale magnetic materials.

Major Program Achievements (over duration of support):
Layered perovskite ruthenates: optical floating zone crystal growth of $Sr_{2-x}Ca_xRuO_4$ for all x, low-temperature specific heat and transport, scanning tunneling micoscopy, electron loss spectroscopy, photoemission, and neutron scattering studies of these materials.
Itinerant electron pyrochlores synthesis of single crystals of $Cd_2Os_2O_7$ and $Cd_2Re_2O_7$, discovery of unique continuous phase transition in $Cd_2Re_2O_7$, detailed investigation of superconductivity at 1.5 K in $Cd_2Re_2O_7$ and metal-insulator transition at 226 K in $Cd_2Os_2O_7$.
Layered vanadates: crystal growth of $K_2V_3O_8$ and NaV_2O_5, observation of Mott-Hubbard gap in NaV_2O_5 using soft x-ray spectroscopy, discovery of novel spin reorientation transition in $K_2V_3O_8$, discovery of giant magnetic field effect on thermal conductivity in $K_2V_3O_8$.

Program Impact:
Our impact is felt in three areas: (1) development of cutting-edge materials with intriguing physical properties, (2) discovery of new phenomena that challenges our understanding, and (3) preparation of high-quality single crystals for in-depth experiments in collaboration with others.

Interactions:
University of Tennessee, University of Kentucky, Clemson University, Florida State University, University of Cincinnati, University of Mississippi, Columbia University, University of Pennsylvania, University of Michigan, Stony Brook University, Boston College, University of Florida, UC San Diego, EPFL Lausanne, McMaster University, Chalk River, ISIS, NCNR, Los Alamos National Laboratory, Princeton University, University of Buffalo, Argonne National Laboratory, Brookhaven National Laboratory.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Medard W. Welch Award, 2001; Chair, Basic Energy Sciences Advisory Committee subpanel for review of Intense Pulse Neutron Source and Los Alamos Neutron Science Center/Lujan spallation sources; selected to BESAC; fellow of the APS; MRS symposium organizer; obtained National Science Foundation funding for three proposals: one focused research group, one individual, and one instrumentation. Approximately 20 invited talks this year.

Personnel Commitments for FY2002 to Nearest +/-10%:
R. Jin (ORNL Postdoc) (80%); D. G. Mandrus (70%); E. W. Plummer (Distinguished Scientist) (20%); B. C. Sales (90%); J. Zhang (Visiting Scientist) (25%); P. Dai (Collaborator)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA $0 **FY01 BA** $0 **FY02 BA** $952K

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0202030

FWP and possible subtask under FWP:
Theory of Condensed Matter

FWP Number: ERKCS08

Program Scope: Research in theoretical and computational materials science and condensed matter physics. The work is focused on the development and extension of modern theories of condensed matter and numerical techniques for applying them and on simulation of complex, dynamical processes. Present emphasis is on highly correlated systems, high-T_c superconductivity, magnetism, neutron scattering in several systems, multiscale modeling of nucleation and growth of carbon nanotubes, magnetic nanosystems, molecular electronics, and various aspects of grain boundaries, surfaces, and interfaces.

Major Program Achievements (over duration of support):
Determination of static and dynamic effects of disorder in 2D antiferromagnets; completion of three review papers on surface diffusion, spin polarons in high-T_c materials, and spin-density waves in Fe/Cr trilayers and multilayers; further development of a theoretical understanding of quantum size effects in ultrathin metal overlayer epitaxy; theoretical understanding of spin diffusion in manganites; mechanisms for the formation of ordered arrays of quantum dots on substrates proposed; computer programs for one- and two-dimensional heat and mass transport in carbon nanotube (CNT) growth formulated and written; electronic structure calculations on CNT initiated; origins of the possible existence of phonon anomalies in MgB_2 predicted and explained.

Program impact:
Provided an explanation of formation of stripes in high-T_c superconductors and other transition metal oxides; work on quantum size effects in metal overlayers on semiconductors stimulated many experimental and theoretical papers; spin diffusion in manganites explained; several *Physical Review Letters*, *Science*, and invited review papers published.

Interactions:
Internal—Center for Computational Sciences, Computer Science and Mathematics Division, Metals and Ceramics Division, Neutron and X-Ray Scattering Groups, Electron Microscopy Group, Surface Physics Group, Center for Nanophase Materials Science, Correlated Electron Materials Group, …

External—Universities of Tennessee, Texas (Austin and Arlington), Florida, Louisville, UC-Irvine, UCLA, Cincinnati, Oklahoma State, Clemson, and Vanderbilt. Strong collaborations and joint papers with several universities and research establishments in China.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Three invited review articles, fifteen invited talks at national and international meetings, several Conference and Workshop Organizing Committees, Fellow of APS (Zhenyu Zhang); tenure track faculty position at UC-Irvine awarded to A. L. Chernyshev.

Personnel Commitments for FY2002 to Nearest +/- 10%:
A. L. Chernyshev (ORNL Postdoc) (90%); A. G. Eguiluz (Joint Faculty Participant) (45%); R. S. Fishman (85%), S. T. Pantelides (Distinguished Visiting Scientist) (10%); K. Varga (ORNL Postdoc) (70%); R. F. Wood (85%); Z. Zhang (75%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $850K **FY01 BA** $774K **FY02 BA** $1034K

Laboratory Name: Oak Ridge National Laboratory

B&R Code: KC0203010

FWP and possible subtask under FWP:
Advanced Ceramics and Thin Films

FWP Number: ERKCS05

Program Scope: Explore the synthesis and properties of thin-films of ion and mixed ion-electron conducting compounds and glasses, in particular lithium electrolytes and lithium intercalation compounds. Elucidate the phase stability and transport properties in relation to the microstructure and composition. Adapt the deposition conditions to control the composition, crystallinity, and microstructure of both the growing film and the underlying interface.

Major Program Achievements (over duration of support):
Microstructure effects of lithium intercalation reactions: Thin films of Li_xCoO_2 are exceptionally stable upon phase transformations and changes in the lattice dimensions when the grain size is below the critical size for stress-induced fracture. When cycled over an extreme composition range, TEM studies of the $LiCoO_2$ film revealed cracks along the crystallographic *c* planes oriented normal to the plane of the film. The ratio of disordered-to-crystalline sites for lithium in nanocrystalline $Li_xMn_2O_4$ films likewise affects the cycling stability and lithium diffusion.

Lithium diffusion studies of thin-film Li_xCoO_2 / Li-electrolyte stacks: For $0.5 < x < 0.9$, the total resistance is largely attributed to the Li transport across the electrolyte film and interface. As x approaches 1, however, the decreasing Li diffusivity in the Li_xCoO_2 films result in a large concentration gradient which varies with the film thickness (5–400 nm) and current density (2 μA–1 mA/cm^2).

Lithium diffusion during plasma deposition: During deposition of a lithium phosphorus oxynitride electrolyte film, a surprisingly large amount of lithium may diffuse into the underlying substrate. Control of the substrate bias during deposition may promote or reverse this reaction. Amorphorization of the underlying surface may also occur during the electrolyte deposition, but does not appear to be a direct consequence of the lithium incorporation.

Program impact:
Provided insight on the ion transport and electrochemical stresses associated with lithium intercalation reactions. Although the $LiCoO_2$ and $LiMn_2O_4$ materials are widely studied, the thin-film architecture and single-phase materials studied in this program prove to be a model system for investigating fundamental properties. The diffusion distances and grain sizes can be varied over a wider range than those accessible for materials of compacted powders.

Interactions:
Department of Materials Science at MIT, Ceramics (Y. M. Chiang, P. Limthongkul)
Department of Physics at Dalhousie University, Halifax NS (J. Dahn)
Department of Physics at University of South Florida (H. Srikanth, R. Hajndl)
Cymbet Corp. Elk River, MN
Electrochemical Systems, Inc. Knoxville, TN (J. Caja)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
International Meeting on Lithium Batteries, June, 2002, invited presentation
Materials Research Society Meeting, April, 2002, invited presentation
Electrochemical Society Meeting, October, 2002, invited presentation (by J. B. Bates)
Invited publications: 2 articles, two book chapters.

Personnel Commitments for FY2002 to Nearest +/- 10%:
N. J. Dudney (group leader) 90%; Y.-I. Jang 100%; G. Veith (post-doc) 80%; I. Dunbar (technician) 60%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $ $831,000 **FY01 BA $**734,000 **FY02 BA $**681,000

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0203010

FWP and possible subtask under FWP:
Chemistry of Advanced Inorganic Materials

FWP Number: ERKCC01

Program Scope:
Synthesis and characterization of novel inorganic materials. Materials currently under investigation include metal oxide nanoparticles and thin-film ceramics, including cuprate superconductors, buffer layers for high-current superconducting films, and optoelectronic materials. Methods of synthesis include wet chemical synthesis of nanoparticles in micelle reactors and sol-gel synthesis of thin films. Novel methods of nanoparticle size selection, such as electrophoresis of derivitized metal particles are under investigation. Techniques for materials characterization include atomic force microscopy (AFM), scanning tunneling microscopy (STM), Rutherford backscattering spectroscopy (RBS), X-ray diffraction (XRD) and various thermal analysis techniques.

Major Program Achievements (over duration of support):
Solution synthetic techniques for a variety of epitaxial oxide films have been developed. Ferroelectric and electro-optic films of layered bismuth oxide containing barium or strontium and tantalum or niobium were prepared. Films of rare-earth oxides, rare-earth aluminates and rare-earth gallates were grown on single-crystal oxide substrates. In addition, techniques were developed which allowed the growth of epitaxial oxides on roll-textured metals and metal alloys as part of the rolling assisted biaxially textured substrate (RABiTS) program. By adapting the polydentate alkoxide chemistry used to prepare thin-films, it has also been possible to prepare oxide nanoparticles in micelle reactors.

Program impact:
Solution synthesis has proven to be a useful technique for the deposition of a number of thin oxide films. It offers precise control of stoichiometry, especially in complex multi-cationic films, excellent thickness control, and good interfacial smoothness. The technique is useful for highly refractory oxides that are difficult or impossible to deposit by vacuum techniques such as evaporation, sputtering or laser ablation. In addition, the technique is considerable less complicated than vacuum deposition. All of these advantages have been exploited in our RABITS program where we have used solution deposition to deposit buffer layers and obtained excellent electrical performance in practical superconductors.

Interactions:
National Laboratories:
ORNL: D. Christen (SSD, superconductivity), G. Jellison (SSD, optics), D. Kroeger (M&C, superconductivity); LANL: S. Foltyn, P. Arnedt (superconductivity); Sandia: P. Clem
Universities:
University of Wisconsin, Madison, Prof. S. Babcock; University of California at Santa Barbara, Prof. F. Lange;University of Tennessee, Knoxville, Prof. Z. Xue; University of Houston, Prof. K. Salama
Industry:
American Superconductor, Inc., Microcoatings Technologies., 3M Corporation, Oxford Instruments

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

R&D 100 Award for contributions to the RABiTS project for the development of practical high-temperature superconductors. DOE Energy 100 Award. Federal Laboratory Consortium Award for Excellence in Technology Transfer. 15 invited talks.

Personnel Commitments for FY2002 to Nearest +/- 10%:
D. B. Beach (Group Leader) 40%; C. E. Vallet 50%; M. Paranthaman 25%; T. G. Schaaff 15% (beginning FY02)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $439,000 **FY01 BA** $428,000 **FY02 BA** $453,000

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 03 01

FWP and possible subtask under FWP:
Structure and Dynamics of Advanced Polymers and Nanophase Blends

FWP Number: ERKCC02

Program Scope: Combining synthetic, experimental and theoretical approaches, we perform fundamental studies of the structure, dynamics and thermodynamics of macromolecular systems to provide a better understanding of the macroscopic properties of advanced polymeric materials. Major experimental tools include a full suite of synthetic methods, including anionic polymerization, small and wide angle X-ray and neutron scattering methods, NMR and neutron spectroscopy, atomic probe and optical microscopies, and state-of-the-art thermal analysis, including temperature modulated DSC and AFM-based microcalorimetry. Simulation and theoretical approaches include molecular dynamics, Monte Carlo, mean field, lattice, and integral equation theory.

Major Program Achievements (over duration of support): The basis of polyolefin blend miscibility has been laid by a combination of coarse-grained and atomistic PRISM theory and molecular dynamics simulation, together with small and wide angle x-ray and neutron scattering studies of homopolymers and polymer blends. Synthetic methods, including anionic polymerization, have been developed to yield polymers of controlled nanoscale architecture such as model block and graft copolymers, nonlinear block copolymer brushes, polymer micelles and polyelectrolytes, with applications as biocompatible materials, routes to controlled drug delivery, self-assembly and templating, and surface functionalization. Unique methods have been developed for the facile synthesis, optical characterization, and simulation of novel polymer nanoparticles and nanorods with tunable quantum electronic, optical, and sensor properties. The discovery of a remarkable, architecture dependent response of block copolymers to process history and shear strain amplitude, impacts block copolymer processing. It points to new strategies for improving block copolymer extrusion, film blowing, and fiber spinning. The development of temperature-modulated calorimetry, TMDSC, where the temperature is varied in frequency and amplitude, has greatly expanded our understanding of the time dependence and distribution of reversible and irreversible phase changes in polymers.

Program impact: Provides insights on the microscopic origins of macroscopic properties of polymer melts, blends, alloys and composites, co-polymers, micellar systems, and small molecule analogs. Investigators include world leaders in the physics and chemistry of copolymers, structure and dynamics of polymer melts, the statistical mechanics and simulation of macromolecular systems, and advanced thermal analysis.

Interactions: National Laboratories: ORNL, ANL, LANL, LLNL, NIST, Sandia; National and international user facilities: IPNS, APS, NSLS, NCNR, LANSCE, ISIS, Risø, Forschungszentrum (Juelich), Saclay; Universities: collaborations/interactions with over fifty US and foreign universities; Industry: Dow, Schlumberger, Medtronic, ExxonMobil, PolyE, 3M, Cummins, ChevronPhillips, Rhodia, Goodyear, Mitsubishi, Dow, National Starch, Avanti Polar Lipids, Du Pont, Roehm GmbH, Shell, Dow-Cargill.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Five APS and one NATAS Fellows; one National Academy of Engineering member; an APS High Polymer Physics Prize winner; two APS Dillon Medals; former president, Neutron Scattering Society of America, three Distinguished Scienists/Professors; two Chairs of APS Polymer Physics Division; DOE-BES Award for Outstanding Scientific Accomplishment in Materials Chemistry; an R&D100 Award; Presidential Green Chemistry Challenge Award; Paul W. Schmidt Memorial Award; Arnold Beckman Award; two ACS Doolittle Awards, and many other awards; numerous regional, national, and international and DOE advisory committee members; twenty journal editorial/advisory boards (Science, PRL, JCP, Macromolecules, J Polym Sci, etc.); 169 refereed papers in last 3 years.

Personnel Commitments for FY2002 to Nearest +/- 10%:
A. Habenschuss (100%), B. K. Annis (100%), B. Wunderlich (FY00-01, ORNL/U. Tenn., 50%), J. W. Mays (FY02, ORNL/U. Tenn., 50%), J. Z. Larese (FY02, ORNL/U. Tenn., 100%), D. W. Noid (50%), B. G. Sumpter (50%), G. D. Wignall (10%), J. G. Curro, (Sandia, 25%), K. S. Schweizer (U. Ill, 20%), F. S. Bates (U. Minn., 20%),

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $1,501K **FY01 BA $1,337K** **FY02 BA $1,743K**

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0203010

FWP and possible subtask under FWP:
Advanced Ceramics and Thin Films

FWP Number: ERKCS05

Program Scope: Explore the synthesis and properties of thin-films of ion and mixed ion-electron conducting compounds and glasses, in particular lithium electrolytes and lithium intercalation compounds. Elucidate the phase stability and transport properties in relation to the microstructure and composition. Adapt the deposition conditions to control the composition, crystallinity, and microstructure of both the growing film and the underlying interface.

Major Program Achievements (over duration of support):
Microstructure effects of lithium intercalation reactions: Thin films of Li_xCoO_2 are exceptionally stable upon phase transformations and changes in the lattice dimensions when the grain size is below the critical size for stress induced fracture. When cycled over an extreme composition range, TEM studies of the $LiCoO_2$ film revealed cracks along the crystallographic *c* planes oriented normal to the plane of the film. The ratio of disordered-to-crystalline sites for lithium in nanocrystalline $Li_xMn_2O_4$ films likewise affects the cycling stability and lithium diffusion.

Lithium diffusion studies of thin film Li_xCoO_2 / Li-electrolyte stacks: For $0.5<x<0.9$, the total resistance is largely attributed to the Li transport across the electrolyte film and interface. As x approaches 1 however, the decreasing Li diffusivity in the Li_xCoO_2 films result in a large concentration gradient which varies with the film thickness (5-400nm) and current density (2μA-1mA/cm^2).

Lithium diffusion during plasma deposition: During deposition of a lithium phosphorus oxynitride electrolyte film, a surprisingly large amount of lithium may diffuse into the underlying substrate. Control of the substrate bias during deposition may promote or reverse this reaction. Amorphorization of the underlying surface may also occur during the electrolyte deposition, but does not appear to be a direct consequence of the lithium incorporation.

Program impact:
Provided insight on the ion transport and electrochemical stresses associated with lithium intercalation reactions. Although the $LiCoO_2$ and $LiMn_2O_4$ materials are widely studied, the thin film architecture and single-phase materials studied in this program prove to be a model system for investigating fundamental properties. The diffusion distances and grain sizes can be varied over a wider range than those accessible for materials of compacted powders.

Interactions:
Department of Materials Science at MIT, Ceramics (Y. M. Chiang, P. Limthongkul)
Department of Physics at Dalhousie University, Halifax NS (J. Dahn)
Department of Physics at University of South Florida (H. Srikanth, R. Hajndl)
Cymbet Corp. Elk River, MN
Electrochemical Systems, Inc. Knoxville, TN (J. Caja)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
International Meeting on Lithium Batteries, June, 2002, invited presentation
Materials Research Society Meeting, April, 2002, invited presentation
Electrochemical Society Meeting, October, 2002, invited presentation (by J. B. Bates)
Invited publications: 2 articles, two book chapters.

Personnel Commitments for FY2002 to Nearest +/- 10%:
N. J. Dudney (group leader) 90%
Y.-I. Jang 100%
G. Veith (post-doc) 80%
I. Dunbar (technician) 60%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $ $831,000 **FY01 BA $**734,000 **FY02 BA $**681,000

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 03 01 0

FWP and possible subtask under
FWP: Structure and Properties of Chain-Molecule Systems Under Shear

FWP Number: ERKCT01

Program Scope:
This program is developing techniques for accurate molecular-based prediction of the structure and properties of systems of long-chain molecules undergoing shear flow, through coarse graining of accurate, atomistic simulations of shorter-chain systems. The coarse graining is based on theory and verified by careful experiments using a newly completed high-strain-rate optical rheometer.

Major Program Achievements (over duration of support):
A novel high-strain-rate optical rheometer has been designed and built, and both rheometry and birefringence measurements have been made at strain rates greater than 10^6 s^{-1}. This instrument has the potential for further advancing the attainable strain rate by as much as 10^2 to 10^3. A nonequilibrium integral equation theory of fluids in shear flow under development has been tested quantitatively against results of nonequilibrium molecular dynamics (NEMD) simulations. Two necessary elements of the new theory have been validated; the third is currently under development. This effort has revealed the form of the hypothetical external field, which can impart the identical structural distortion to the configuration of fluid molecules as does shear flow. NEMD simulations have been performed of long-chain polymer melts in shear flow and of lubricant molecules sheared between narrowly confining surfaces. Equilibrium, transient shear, and steady-state shear structure and properties have been determined.

Program Impact:
Non-Newtonian flow properties of complex fluids such as long-chain polymers and lubricants are poorly understood and are of great importance in many applications. The combination of cutting-edge experiment, theory, and simulation in this program advance the fundamental knowledge both quantitatively and qualitatively. The ultimate objective is a quantitative, predictive tool for the dynamical properties and microstructures of polymer solutions and melts during processing and lubricants in severe service.

Interactions:
Because the budget for this program is small, its approach is almost totally collaborative. The experimental effort has been performed in collaboration with Prof. M. D. Dadmun, postdocs, and graduate students from the U. of Tenn. Samples have been prepared in collaboration with V. J. Krukonis of Phasex Corp. Birefringence experiments have been performed in collaboration with G. E. Jellison of the ORNL Condensed Matter Sci. Div. Theory has been developed in collaboration with Prof. Yu. V. Kalyuzhnyi of the U. of Lviv, Ukraine, and Prof. S. T. Cui and graduate students from the U. of Tenn. NEMD simulations have been performed in collaboration with Prof. Cui, Prof. P. T. Cummings of Vanderbilt U., and graduate students of the U. of Tenn. This program led to a separate collaborative research project by Prof. Cummings with Mobil Research on lubricant performance at high pressure. During this period the program resulted in eight publications in peer-reviewed journals, with two more submitted and three more currently in preparation.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
AIChE Alpha Sigma Chi Award, P. T. Cummings. AIChE Fellow, H. D. Cochran.

Personnel Commitments for FY2002 to Nearest +/- 10%:

H. D. Cochran	ORNL PI	10%
S. T. Cui	UT Res. Assoc. Prof.	25%
Yu. V. Kalyuzhnyi	UL Prof.	10%
K. S. Mriziq	UT PhD student	100%
C. Baig	UT PhD student	100%

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $224k **FY01 BA** $229k **FY02 BA** $217k

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Nucleation, Growth, and Transport Phenomena

FWP Number: ERKCT02

Program Scope:
Development and application of nanoparticle and molecular assembly approaches for bottom-up fabrication of nanomaterials and nanosystems. Fundamental studies of nucleation, growth, and transport phenomena involving particle/cluster formation in homogeneous reactive solutions and at solution-substrate interfaces as well as nanophase/heterostructure evolution during synthesis and processing. Utilization of national facilities at ORNL, including small-angle and dynamic scatterings, in-situ diffractions, and high resolution electron microscopies.

Major Program Achievements (over duration of support):
(1) Homogeneous synthesis of nanoparticles and crystals: Clarified the gel-to-crystal transformation mechanism during early-stage zeolite synthesis. Developed a microwave synthesis approach for synthesis of monosized silicalite nanocrystals. Developed dielectric-tuning and refluxing methods for producing nanoparticles (barium titanate). Elucidated the initial processes of nanophase formation during the classical sol-gel reactions.
(2) Nanocrystallization in solid phases: Discovered a hydrate-based transition phase during gas transformation of molybdenum oxide to nanocrystalline nitride. Developed a seeded polymer coating approach for fabrication of nanocrystalline yttrium-stabilized zirconia films stable at temperature up to 1200^{o}C. Developed a vapor-phase conversion method for nanostructured zeolite membrane fabrication. Obtained high-temperature XRD data for mixed-ionic conducting perovskite-type oxide membranes.
(3) Heterogeneous growth of nanostructures: Discovered aluminosilicate particle monolayer formation and amorphous-to-cancrinite phenomena on a stainless-steel surface. Investigated the particle-surface interaction forces during biomimetic deposition of ceramic films on self-assembled molecular monolayer grafted on various substrates.
(4) Developed a new approach for growing long silica microfibers and functional anisotropic monoliths via combination of pulsed electric field with a sol-gel reaction.

Program impact:
Provided insights and new approaches for controlled fabrication of nanostructured materials in the form of monodispersed ultrafine particles, quantum dots, films or coatings, inorganic membranes, and nanophase monoliths. Potential impacts upon development of nanophase ceramics, advanced catalysts, fuel cell and solar cell energy materials, next-generation nanodevices, medical applications, and DOE waste management.

Interactions:
Internal— High-Temperature Materials Laboratory (HTML) User Facilities; SAXS User Facility; many individuals. External—Purdue Univ. (M. Harris); Case Western Reserve Univ. (M. DeGuire); Clemson Univ. (B. Lee), North Carolina A&T Univ. (K. Roberts); Univ. of New Orleans (D. Hui); Univ. of Cincinatti (Y. Lin);

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
First-Place Winner, poster competition in 102nd ACerS annual meeting (2000); Journal Cover, *J. Mater. Sci.* (2000); Technical Achievement Award**,** honored by ORNL (UT/Battelle LLC) (2000); Award of Excellence, honored by Society for Technical Communications (2001); Associate Editor, *J. Nanosci. Nanotechnol.* (2002); Guest Professorship, honored by South China Univ. of Technol. (2002); Chair/Co-chair for 5 symposia in nanomaterials and nanotechnology; 4 Keynote Speeches, 5 Invited Lectures, more than 15 invited talks since 2000

Personnel Commitments for FY2002 to Nearest +/- 10%:
M. Hu (~30%), L. Pozhar (visiting professor, 60%), X. Wang (grad. student, 25%)

Authorized Budget (BA) for FY00, FY01, FY02:
FY00 BA $220,000 **FY01 BA $**198,000 **FY02 BA $**190,000